TRANSFER OF HEAVY METAL POLLUTANTS FROM LAKE ERIE BOTTOM SEDIMENTS TO THE OVERLYING WATER

by

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INTRODUCTION TO THE HEAVY METAL POLLUTION PROBLEM

Mercury

Studies of mercury consumption in the United States (FWQA, 1970) showed that two main industries accounted for a majority of this consumption, the manufacture of electrical apparatus, and the use of mercury cells in the electrolytic production of chlorine and caustic soda. The consumption of the latter industry was due in part to the charging of new installations, but the bulk of this mercury (FWQA, 1970, p. 10) was required to replace losses. Both the BASF Wyandotte Chemical Corporation, Wyandotte, Michigan, and Dow Chemical Corporation, Sarnia, Ontario, were chlor-alkali producers using this type of electrolytic cell. According to data presented by FWQA (1970, pp. 77-86), the Wyandotte Chemical Corporation installation at Wyandotte, Michigan, was by far the largest consumer of mercury among industries in the Detroit River-Western Lake Erie area. High consumption was also noted for the Detrex Chemical Corporation chlor-alkali facility at Ashtabula, Ohio. FWQA (1970) and OWRC (1970) cited these plants as having discharged mercury in amounts of 10 to 195 lbs /day. By April 26, 1970, following intensive efforts to eliminate mercury losses, each of these three plants was reportedly discharging less than 2 lbs /day.

Numerous other general sources of pollutant mercury also became known and were reviewed in some detail by D'Itri (1972). Besides numerous industrial uses, mercury is also used in agricultural fungicides, dental preparations, and a host of

diversified products. According to Joensuu (1971), the amount of mercury released from fossil fuel combustion is approximately one order-of-magnitude greater than that released by weathering of rock material, and is a quantity comparable to that emitted by industrial waste processes. Mercury from this source, however, is subject to widespread atmospheric dispersion, as evidenced by its record in the Greenland Ice Sheet (Weiss, et al., 1971), and hence may not be too significant in lacustrine pollution.

Since the initial flurry of activity which occurred soon after mercury contamination had been discovered in Lake Erie, several studies have more closely defined the extent and nature of the contamination in this lake. Kovacik (1972) sampled surface, middle, and bottom waters and sediment cores and grab samples on a five-minute latitude-longitude grid in the Western Basin. He found no significant vertical or horizontal variations among the water samples, which were analyzed unfiltered and found to contain mercury in amounts of 0.1-0.2 µg/l. Bottom sediment samples, however, contained 0.026 to more than 3.0 ppm (dry weight basis), and the major pattern of dispersion clearly pointed to the Detroit River as the chief source. Due to the lack of data for a few key unsampled stations, however, the source of a second area of apparent mercury contamination, located north of Pelee Island and extending north to the Canadian shore, could not be confidently ascertained. Walters et al. (1972) and Walters and Herdendorf (1973) used statistical means to compare the mercury content in bottom sediments to the chemical parameters of the overlying water masses, and were able

to demonstrate a good correlation between them. Kovacik (1972) and Kovacik and Walters (1973) found that in the sediment column two zones of mercury concentration existed. Below a depth of about 15 cm the mercury content was fairly constant and low (0.04-0.09 ppm); above this depth it increased rapidly to surface values of 1-4 ppm.

Chromium and Nickel

The possibilities of other heavy metals creating pollution problems were evident almost as soon as the extent of the mercury problem was realized (FWQA, 1970, p. 44). Chromium and, to a lesser extent, nickel were among the possible candidates to be future pollution problems. Although employed to some extent in alloys, refractories, tanning of leathers, and as a slimicide, chromium finds its major use in the electroplating industry (Kirk-Othmer Encyclopedia of Chemical Technology, 1947, vol. 3, pp. 935-940). The major use of nickel is in alloys, but it too is extensively used in electroplating, where its technology and use is strongly wedded to that of chromium.

Due to a number of technical difficulties not solved until 1926, and also because of several years of delay due to court battles over patent rights, chromium electroplating did not become extensively available on a commercial basis until the late thirties, when the industry experienced rapid growth. Concomitant pollution of natural waters by electroplating effluents was an early problem to industrial engineers. Among the effects noted at the time were a persistent yellow color in

the natural water courses receiving such effluents and interference with the natural biological processes of stream and sewage self-purification (Hoover and Masselli, 1941, p. 131). As chromium was a very valuable material, there was some economic incentive to institute recovery measures. Even so, some treated effluents still contained chromium in amounts ranging from 102 to 247 mg/l (Hoover and Masselli, 1941, pp. 132-133).

The number of possible contributors of pollutant chromium and nickel to the Detroit River-Lake Erie system has been found to be very large. Since electroplating plants were the most likely sources, a check of the Yellow Pages of the telephone directories of the four largest cities on the lake system yielded 120 listings for Detroit, 106 for Cleveland, 21 for Buffalo, and 19 for Toledo. Even though these listings may not represent all firms or plants doing electroplating in the given areas, it is almost certain that they include the vast majority, and it seems safe to conclude that the industry in the Lake Erie region is essentially concentrated in the cities of Detroit and Cleveland. Hence, it is expected that these are the major source areas for pollutant chromium and nickel entering Lake Erie.

FWQA (1970, pp. 45-48) presented some data on these metals in Lake Erie sediments which support the above conclusion. Chromium contents of up to 200 ppm (dry weight basis) and nickel contents in excess of 100 ppm were found near both cities, as compared to contents of 10-30 ppm chromium and 20-40 ppm nickel

in other areas. Unusually high values of chromium (but not nickel) also were found near the mouth of the Ashtabula River (910 ppm) and at the mouth of the Buffalo River (260 ppm). To date, however, no extensive studies on the distribution of these metals in Lake Erie have been published.

Major Questions

Heavy metal pollution in any lacustrine environment immediately raises a number of questions concerning man's future ability to make use of valuable lacustrine resources, such as fresh water, food sources (mainly fish), and recreation areas. Many of these questions are of a dominantly biological or ecological nature, and concern such factors as toxicity thresholds and food chain concentration of toxic pollutants. Others are more sedimentological and geochemical. All, however, are closely tied together, and classification by classical scientific disciplines is very arbitrary.

It is more useful, therefore, to consider these questions within the lacustrine portion of the general sedimentary cycle. Basically, four stages occur within this cycle: 1) introduction of the pollutant into the lacustrine environment, 2) physical transportation and dispersal within the lake basin, 3) transfer out of the lake water mass, mainly through sedimentation and burial, but also to some extent by vaporization losses to the atmosphere, and 4) post-depositional transfer of buried pollutant back across the sediment-water interface into the overlying lake water mass. Investigation of the post-depositional transfer of pollutants is the major objective of this study.

In the introduction stage, the pollutants enter the lacustrine system. The most important sources for heavy metal pollutants are likely to be industrial outfalls, rivers carrying industrial effluents, and municipal sewage outfalls.

The second stage basically encompasses the time of residence of the pollutant within the water mass of the lake. During this stage the pollutant runs the highest risk of being incorporated into the biosphere and subsequently concentrated via food chains. Physical processes, mainly current action and eddy diffusion, transport the pollutant and disperse and dilute it. A major task is to elucidate the transport phases and chemical speciation of the heavy metal pollutant, and also to determine the mechanisms and patterns of dispersal.

The third stage consists of processes of removal of pollutants from the water mass. Here the dominant process is sedimentation, and the main questions are kinetic in nature. Since biological activity in a lacustrine system essentially ceases a few centimeters into the sediment column, burial offers a convenient natural process of cleansing the overlying water mass and the overwhelming bulk of the biosphere. Obviously, the more strongly a heavy metal pollutant is held by sediment particles and the faster the sedimentation rate, the better this process of removal will work. Here again some knowledge of the transport phases, plus information on the rates of sedimentation is essential.

The fourth stage, the transfer of buried pollutants back across the sediment-water interface into the overlying water mass, poses the most difficult questions. Several processes

from the industrial chemical literature to provide information on pollutant sources, especially the times of major plant openings and relative discharges, and this information was used in conjunction with other data from the literature, the experimental phase data, and 21 detailed depth profiles of each metal from sediment cores taken in various locations throughout the lake to put together an interpretation of the pollution problem regarding these metals in this lake. The ultimate goal was to make predictive statements and recommendations regarding this pollution problem.

TRANSPORT PHASES OF MERCURY, NICKEL, AND CHROMIUM IN LAKE ERIE WATERS AND SEDIMENTS

Knowledge of the transport phases was shown in the preceding discussion to be crucial to developing an understanding of the behavior of a heavy metal pollutant after its introduction into the lacustrine environment. In this section the available data from the literature are briefly reviewed and summarized to gain an understanding on this point.

Although mercury is known to be introduced into rivers and streams in a wide variety of forms, it apparently quickly becomes either precipitated or adsorbed onto sediment particles (Jenne, 1970). A large number of mercury analyses of natural waters have been published and it seems clear that, except in the immediate vicinity of outfalls, the mercury content of waters is so low that transportation in aqueous solution by moving water masses is essentially negligible (see the review by Krenkel, 1973, pp. 319-320). Kovacik (1972) and Chau and Saitoh (1973) analyzed water samples from the Western Basin

of Lake Erie and the Great Lakes, respectively, and found extremely low mercury contents, on the order of 0.1-0.2 µg/l. The actual mercury content of most waters may well be one or two orders-of-magnitude lower than commonly reported values.

The high mercury contents of sediments immediately underlying such "clean" waters leave little doubt that newly released mercury is quickly and almost quantitatively incorporated into or onto sediment particles. Cranston and Buckley (1972) showed that suspended particulate matter taken from a polluted river-estuary system in Nova Scotia contained mercury in amounts of up to 34.4 ppm (dry weight basis). The major transport phases are clearly solid sediment particles, but the mode of binding and the distribution of the mercury among the various sediment components is unknown. Many investigators have found evidence that mercury, among other heavy metals, tends to be preferentially concentrated in the fine sediment fraction and associated with organic carbon or sulfur which is concentrated in the fine sediment fraction (Cranston and Buckley, 1972; Kennedy et al., 1971; Thomas, 1972; and Vernet and Thomas, 1972a).

Only one study involving a true chemical partitioning analysis of naturally occurring sediments for mercury seems to have been conducted prior to this work. Cline et al. (1973) developed and used a partitioning analysis in a study of the mechanisms of mercury dispersal in the Lake St. Clair-St. Clair River system. The mercury in sediment samples from six stations taken moving downstream from the source (Dow Chemical of Canada, Ltd., chlor-alkali operation at Sarnia, Ontario) was partitioned among 1) KCl-extractable, adsorbed mercury, 2) H_2O_2-digestible

organic-mercury complexes, and 3) $KMnO_4$-digestible refractory organic complexes and inorganic precipitates bearing mercury. A high correlation was found between the amount of organic mercury (nearly the total amount of mercury at each station) and the total amount of organic carbon. This study suggested that mobilization of the mercury was by means of a particulate organic sediment fraction of low specific gravity.

Assuming most of the mercury in a given lacustrine environment is in the organic form as suggested by Cline et al. (1973), then the distribution of the pollutant should essentially follow current patterns and be dispersed and buried according to the known general principles of sedimentation. Walters et al. (1972) and Walters and Herdendorf (1973) showed that in the Western Basin of Lake Erie mercury in the bottom sediments was widely distributed over the whole area, and that this distribution closely followed the patterns of movement of the main water masses. Similarly, the data of Thomas (1972) showed a widespread movement of mercury out of the Niagara River source area covering a vast expanse of the bottom of Lake Ontario. In the above investigations the mercury was concentrated in the more quiet and deeper basinal areas. Thomas (1972) corrected his data for quartz dilution, however, and clearly demonstrated increasing gradients back to the source. Conversely, then, pollutant metal loadings themselves may be useful as tracers in studying the sedimentation patterns and processes in lakes.

The first indications that buried mercury might be remobilized and cross back over the sediment-water interface came with the discovery that micro-organisms in the sediments are

capable of methylating mercury (Jensen and Jernelöv, 1967, 1968, 1969; Wood et al., 1968). The two methylated forms, monomethylmercuric ion (CH_3Hg^+) and neutral dimethylmercury (CH_3HgCH_3) are much more labile than nonmethylated forms. Dimethylmercury is the more mobile and volatile of the two, however, and both are extremely toxic, in part due to their ability to cross biological membranes impervious to most toxins (Study Group on Mercury Hazards, 1971).

The various factors influencing biological methylation of mercury have recently been reviewed by Fagerström and Jernelöv (1972). The main biochemical pathway appears to be transfer of a methyl group from methylcobalamin (methylated vitamin B_{12}) to inorganic mercuric ion (Wood et al., 1968). Under strongly anerobic conditions, methylcobalamin is produced by methanogenic bacteria as a component in the synthesis of methane. Consequently, it is under these conditions that mercury methylation occurs at the greatest rate. Also, because methylation is an in vivo process, it varies strongly with general microbiological activity and availability of nutrients, and it follows the Q_{10} rule (doubled rate when the temperature is raised 10°C). The pH is apparently the dominant factor in determining the methylated form produced by this process. Strongly alkaline pH tends to favor the production of the more volatile dimethylmercury, while acidic to slightly alkaline pH favors the formation of the monmethylmercuric ion. Methylation is known to be inhibited by the presence of sulfide due to precipitation of the mercury as mercuric sulfide and its consequent unavailability to organisms.

Much of the interest in mercury pollution stemmed from the discovery of the methylation process taken in the light of the epidemic poisonings at Minimata, Japan. Large segments of the populace there had been poisoned by eating shellfish taken from Minimata Bay. The cause of the poisoning was eventually determined to have been monomethylmercury contained in the shellfish, and the source of the mercury was found to be a plastics factory in Minimata which had discharged its wastes into the neighboring bay. Unlike the mercury discharged from chlor-alkali plants, which is inorganic, the discharges from the Minimata plastics factory had included substantial amounts of methylated mercury. Thus, at Minimata the role played by microbial methylation in the sediments in relation to the poisonings was actually somewhat obscured.

Some recent studies on the rate of methylation in bottom sediments have indicated that sediment cover may be sharply depressing the efficiency of microbial methylation, and that therefore in many contaminated areas this process may be nearly negligible in at least some aspects (Jernelöv, 1970). The results showed that the rate of microbial methylation in the cores containing only microorganisms fell off sharply with depth and was essentially nil when the mercury-loaded layer was deeper than four cm. However, when burrowing organisms were present, methylmercury was released from sediments up to 10 cm depth. Bongers and Khattak (1972) investigated the effectiveness of sand and gravel to decrease methylmercury release and found that six cm was the maximum effective depth even in the presence of Tubificidae.

Evaluation of the consequences of methylation in bottom sediments then in large part reduces to a question of kinetics, pitting the rate of methylation against the rate of sedimentation. For example, Jernelov's (1970) data suggested that in the presence of Tubificidae, methylation proceeds at an approximate rate of 0.5% per year of the total mercury in the sediment. Using a value of 1.0 cm/yr as being representative of the rate of sediment accumulation in Lake Erie, one may then note that since methylation under such conditions essentially ceases at a depth of 3.0 cm, a time period of roughly 3 years would then be required for cessation of this process. Approximately 1.5% of the original mercury would have been mobilized by this process, but roughly 98% would have been permanently buried, barring of course such occurrences as storm action or dredging. Therefore, it seems possible that in many lakes mobilization of mercury by means of methylation may be insignificant in terms of resource use, and that natural sedimentation processes may suffice to remove the mercury from the lacustrine ecosystem following pollution abatement measures at the sources.

Another process for the mobilization of buried mercury involves the breakdown via diagenetic redox reactions of large, insoluble mercury-organic complexes into smaller, soluble mercury-organic complexes. If the degree of redox reactions is extensive, breakdown of the organic portion of the complexes might reach completion, leaving free inorganic forms. This seems unlikely in a lacustrine system, however, and certainly is not necessary to generate movement, as was implied by Cline

and Upchurch (1973). These authors proposed a model in which the diagenetic degradation of metal-organic complexes released the metal, which diffused upward or was carried upward on bubble interfaces, to be re-complexed by the active functional groups still present in the fresh organic material in the upper layers of the sediment column.

Little information is currently available as to which organic components are the most important in the overall organic transport phase. In terms of predictive value, as far as the eventual diagenetic stage is concerned, it would be well to know more about the mercury distribution within the overall organic component, as the degree of susceptibility of various kinds of organic matter to diagenetic degradation varies considerably. Partly because of the above consideration and partly because the transport phases of mercury in Lake Erie might be somewhat different than those in other bodies of water, it was decided that an experimental phase partitioning of some Lake Erie sediments was in order.

Phase Partitioning Analyses of Lake Erie Materials

Because of the lack of sufficient data on the transport phases of and mechanisms involving mercury in the lacustrine environment, and also because of the uncertainty of the validity of applying directly to Lake Erie, certain concepts derived in studies in other areas, it was deemed necessary to perform experimental phase partitioning analyses on sedimentary materials taken from and, hopefully, representative of this particular lake. This study had several objectives which were crucial

to later interpretation of metal depth profiles in the sediment column and of the horizontal distribution data concerning mercury in the surface (bottom) sediments. The first goal was to check the normal surface water and the surface microlayer (if any) for dissolved mercury. Kovacik (1972) had reported that unfiltered surface waters of the Western Basin of Lake Erie contained roughly 0.1-0.2 µg/l of mercury, and also that bottom waters had basically the same mercury content. It was desired to check for dissolved (defined here as the ability to pass through a 0.45 µ millipore filter) mercury primarily for comparison with the dissolved contents of interstitial waters. Since there had been much speculation in the literature concerning mercury's ability to migrate upward after burial, it was hoped that a definite concentration gradient within the interstitial water implying an active diffusion mechanism, might be detected in this manner. Thirdly, a phase partitioning of the mercury in the surface sediments was desired to check some of the proposals of Cline et al. (1973) in regard to the transport mechanism during the time interval between introduction and burial of the pollutant mercury. Lastly, a similar partitioning of some deeply buried sediment samples containing only background concentrations of mercury was performed to allow comparison with the upper, polluted ones. It was proposed that such a comparison would yield clues regarding both 1) the changes in phase distribution due to increased mercury concentration (pollution) and 2) changes in the mercury-carrying phases themselves due to the effects of burial and diagenesis, thus giving more information with regard to the possible process or processes

causing upward migration.

The necessary samples were obtained on a one-day cruise in the Islands area of the Western Basin of the lake aboard the R/B BIO-LAB on June 22, 1973. Three sampling stations (B1: 41°35'N 82°55'W, B2: 41°40'N 82°55'W, and B3: 41°40.2'N 82°50'W) were visited. Water samples were taken at each station ten centimeters below the surface. These water samples were stored in one-liter polyethylene bottles without being acidified or treated in any special way. Sediment samples were obtained using a Peterson dredge and also by using a hand-driven coring device described by Kovacik (1972, p. 13). Triplicate core sets were taken at each station, and all cores and grab samples were immediately placed under refrigeration in an ice chest. Upon return to the laboratory they were transferred to a refrigerator and stored near 4°C.

Surface Water Analyses

The water samples were analyzed immediately upon return to the laboratory, and the analyses were completed within seven hours of the first sample collection. The water samples were pressure filtered through 0.45 micron filters to remove particulate matter - prior to analysis of each sample for mercury which was performed in triplicate using the flameless atomic absorption spectrophotometry (FAAS) method described by Kovacik (1972, pp. 16-20). As a special precaution in view of the low concentrations expected, all of the glass reaction vessels used had been soaked 24 hours in 1.0 N HNO_3 and before each was used a blank determination was run using it to insure that no mercury

was contributed via glass desorption of mercury loaded onto vessel walls.

Every water sample gave a perfect blank response. Under the conditions of analysis and AAS machine behavior at the time, it was estimated that the detection limit was 0.02 µg/l. Therefore all that could be said was that there was less than this concentration in all of the samples. Very little particulate material was found on the millipore filters, and it was decided not to analyze the particulate/filter composites because the filters used were known to contain mercury in highly variable amounts in relation to the amount expected to be contributed by the particulates; i.e., a valid correction for filter mercury could not have been attained.

Interstitial Waters

Two cores (B1, #1 and B2, #1) were selected for interstitial water analysis. Each was sectioned into four ten- or twenty-centimeter intervals and interstitial water was extracted by centrifuging the samples at 8000 rpm for 15 minutes at 4°C in a refrigerated ultracentrifuge. Under these conditions, almost all particulates were sedimented, and the net result was similar to filtration. Each extract was measured for volume and analyzed for mercury by the same procedure as for the other water samples, except that a more rigorous oxidation step was employed. First, five ml of concentrated H_2SO_4, ten ml of concentrated HNO_3, and two ml of 5% $KMnO_4$ were added to the reaction bottles. After ten minutes no loss of color from the permanganate had occurred in any of the samples; then 0.1 g sodium persulfate

was added to each sample to assure complete oxidation. The samples were swirled and allowed to sit for thirty minutes. No heating was applied due to the possible risk of volatilization of the small amounts of mercury expected. The samples were then reduced and run in the usual manner.

The results, summarized in Table 1, show that no mercury was detected in the interstitial water extracted from the core sediments. The concentrations were less than the detection limit, which was corrected for each sample according to the volume of interstitial water analyzed. Because these small sample sizes raised the effective detection limit, and because it was still thought that a measurable amount of dissolved mercury might be present in the upper ten centimeters of the sediment column, interstitial water samples were also extracted from the corresponding grab samples (GSB1 and GSB2). The greater amount of sediment available from these grab samples allowed triplicate 100-ml samples to be extracted and analyzed. The analyses were performed in the same manner as before, and the results are summarized in the bottom portion of Table 1. The extracts from GSB1 showed no mercury as before, and accordingly the concentration reported is less than the detection limit (0.02 - 0.03 µg/l). On the other hand, the samples from GSB2 showed a definite, although extremely low mercury content (0.04 - 0.08 µg/l).

TABLE 1

Results of interstitial water analyses in cores and grab samples taken near the Islands area of Lake Erie.

Sample	Sample volume, ml	Response, µg Hg	Hg, µg/l
Core B1, #1			
0-10	29	<0.002	<0.07
10-20	22	<0.002	<0.10
20-30	24	<0.003	<0.12
30-40	21	<0.003	<0.15
Core B2, #1			
0-10	45.8	<0.002	<0.04
10-20	36.7	<0.003	<0.08
30-50	57	<0.002	<0.04
50-70	34.2	<0.004	<0.12
Grab sample GSB1	100	<0.003	<0.03
	100	<0.002	<0.02
	100	<0.002	<0.02
Grab sample GSB2	100	0.008	0.08
	100	0.005	0.05
	100	0.004	0.04

These results demonstrate that a concentration gradient in these sediments is essentially undetectable. Hence, the flux of mercury due to post-depositional migration via a diffusion mechanism must be very small. The very slight concentration noted in the GSB2 extracts does indicate the possibility that a concentration gradient may be localized in the sediment column at that geographic location from which this sample was taken and only within the uppermost few centimeters of the sediment column.

Sediment Sample Partitioning

A suite of six sediment samples was selected for the phase partitioning analysis. Four of these were taken from the cores used in interstitial water anslyses. The samples B1, #1, 0-10 cm and B2, #1, 0-10 cm were selected to represent modern, pollution-loaded bottom sediments typical of much of the Western Basin. Two deeper intervals of the same cores, B1, #1, 60-70 cm and B2, #1, 50-70 cm, were chosen to represent more deeply buried, background (prepollution) sediments. The remaining samples were grab samples (GS1, from near Monroe, Michigan and GS32, taken from the harbor at Buffalo, New York) which had been collected on a September 1972 cruise aboard the R/V INLAND SEAS.

Total mercury and water content of the six samples were determined by the FAAS procedure given by Kovacik (1972, pp. 20-22). Then five-gram portions of wet sediment from each sample were weighed into tared 250-ml centrifuge bottles and subjected to extractions with seven reagent solutions. After each extracting solution had been separated from the sediment in the centrifuge bottles by means of centrifugation at 5000 rpm for 15 minutes at 4°C, the solution was poured off into a 250-ml Erlenmyer flask and subjected to an oxidation procedure. Five ml of concentrated H_2SO_4, fifteen ml of concentrated HNO_3, and one to three ml of 5% $KMnO_4$ were added to each extract and placed under low heating on a hotplate. Extra $KMnO_4$ was added as necessary to maintain a purple color. Once this had been maintained for five to ten minutes, an addition of 0.1 g sodium persulfate was made to insure oxidation, and the solution was

allowed to react on the hotplate for forty minutes. After cooling to room temperature, the contents of the flask were brought up to the 150-ml by addition of double-distilled water, and were then reduced and run in the usual manner. At two points during the run, the centrifuge bottles were connected directly into the FAAS analyzing circuit to check for possible presence of metallic mercury. One of these checks was to see if any naturally volatile metallic mercury was present; the other was performed immediately after addition of a reducing solution, and was designed to detect any metallic mercury which might have been amalgamated to hydrous iron oxides as had been suggested by Jenne (1970).

Volatile Metallic Mercury

After the five wet grams of sample had been weighed out, 100 ml of double-distilled water were added and the sediment was suspended using a rubber policeman. The bottle was then directly connected into the analyzer circuit of the FAAS unit and the response was recorded in the usual manner. Although it was known that some volatile compounds likely to be present in the samples (such as H_2S) might cause absorption in the light beam of the instrument, no responses at all were obtained. Therefore, it was concluded that 1) there was no interference by other volatiles, possibly because of absorption by the anhydrone drying tube in the circuit and 2) no volatile metallic mercury was present in the samples.

Ion-exchangeable Mercury

After centrifugation and removal of the water, 100 ml of

1.0 N $MgCl_2$ solution were added and the mixture was suspended with a rubber policeman and allowed to react for two hours with periodic shaking. Two reagent blanks were also run in exactly the same manner as the samples and showed a mean blank value of 0.025 µg of mercury. In the four samples from the Islands area the sediments absorbed this blank and gave a zero gross response. Grab sample GS1 gave back this blank within analytical error, and only grab sample GS32 showed a small net response (0.003 ppm, dry weight basis). The blank absorptions explained in part why no mercury had been detected in the corresponding interstitial waters. This blank absorption factor seemed to be related to the total mercury content of the various samples. Grab samples GS32 and GS1 contained 2.13 and 3.38 ppm total mercury respectively (total assay method, dry weight basis); these contents are more than twice those taken from the four core samples. Therefore their available binding sites likely had already been saturated, whereas such sites were still available in the less-contaminated core samples.

Strong (0.2 N) NaOH Extracts

The sediment samples were next extracted with four to five successive 80-ml portions of 0.2 N NaOH (pH = 13.25). The first extracts were quite brown in color, but diminished to colorless by the fifth extract. A parallel decrease in mercury content was noted. Upon addition of the sulfuric acid in the oxidation stage, much of this brown material precipitated. These extracts apparently included both humates (which precipitated) and fulvates (which did not). A rather high mean

blank value of 0.060 µg of mercury was noted for this type of extraction. As the results in Tables 2 and 3 show, this series tended to include significant amounts of mercury in the samples with high total mercury.

Weak (0.005 N) NaOH Extracts

Additional organic matter was extracted with seven to eight 80-ml portions of 0.005 N NaOH, which resulted once again in a strong brown color in the initial extracts. As in the previous series, mercury in the extracts fell off with the decrease in brown color. The pH of this solution prior to extraction was measured at 11.45. As in the earlier series, the initial addition of sulfuric acid produced precipitation of brown organic material, this time to a greater degree, however. The results in Tables 2 and 3 show, that this series removed much of the mercury content of each of the six samples. Analyses of reagent blanks showed a mean mercury content of 0.045 µg.

Weak (0.005 N) Acetic Acid

Only one extraction was performed in this series. Eighty-ml of 0.005 N acetic acid (pH = 3.73) were added to each sediment sample. In all six samples the extracted solutions were crystal clear and gave back, easily within analytical error, the mean blank value of 0.012 µg.

Amalgamated Mercury

Fifty ml of a solution made 2 M in phosphoric acid and 0.50 M in hydroxylamine hydrochloride were added to each sample in this series. This solution is strongly reducing and quite

acidic, and was designed to destroy hydrous oxides of manganese and iron. Tests on artificial hydrous iron oxides showed that this solution would dissolve quantities greater than those likely to be present in the sediment samples within a reaction time of twenty to thirty minutes at room temperature. Jenne (1970, p. 44) had suggested that metallic mercury might be amalgamated with hydrous iron oxides in natural sediments. Immediately after addition of the reagent solution, each plastic bottle was again directly connected to the analyzer circuit and run for ten to twenty minutes to test for such a component. No responses were detected, so it appeared that Jenne's speculation was incorrect, at least for these six samples.

Reducible Phases and Organic Bases

The solution used in the above stage was extracted, poured off, and initially oxidized by adding small amounts of solid potassium permanganate until the purple color stabilized, indicating neutralization of the hydroxylamine hydrochloride. The solution was then oxidized and analyzed. Two blanks were also run and gave a mean blank response of 0.077 µg of mercury. Only sample GS32 showed a significant response; it also differed from the other samples in that its extract had a yellow color similar to that generated when the reducing solution was tested with artificial hydrous iron oxides. Therefore a second extraction of this type was performed on this sample; it came out clear. The samples were washed once with 100 ml of double-distilled water, centrifuged, and the wash water was analyzed. Strangely enough, higher responses were found in the wash waters,

and the interpretation of this phenomenon is given in the discussion of the next extracting procedure.

EDTA Extractable Mercury

Eighty-ml aliquots of 0.1% disodium ethylenediaminetetraacetate were applied to the samples in this series. In the early extractions, the solutions came out slightly brownish in color, and minor precipitation of brown organic material occurred when the sulfuric acid was added in the oxidizing step. Two to five extractions were necessary to achieve clarity in the extracts. A first wash of 100 ml of double-distilled water also came out slightly brownish in color and exhibited similar behavior. A second such wash then came out clear. Reagent blanks of the EDTA solution showed a mean blank contribution of 0.035 µg of mercury. After correction for blank contributions, it was apparent that the two washes contained about as much mercury as was removed by the EDTA extracts themselves. Because these solutions were apparently removing organic material similar in some respects to that obtained in the NaOH extractions, it was believed that the extraction by the EDTA was an indirect one. That is, because the EDTA solutions were acidic (pH = 4.90) and of similar pH to the acetic acid solutions (pH = 3.73) which had failed to extract anything, the EDTA probably solubilized these organics by removing from them metal cations which were keeping them in the form of insoluble complexes. Then part of the decomplexed organics, probably still containing most of the mercury, went into solution. When the first wash was added, the less acidic pH must have promoted the solubility of the re-

organically bound mercury. As shown in the results summarized in Tables 2, 3, and 4, not much mercury was found in one treatment with this extracting agent. Slight increases in mercury response were noted, however, for samples GS1 and GS32, which contained the highest total mercury in the six-sample set. The pH of the dithiothreitol solution was 6.55, the same as that of the double-distilled water which was used. Reagent blanks had a mean mercury response of 0.035 µg of mercury.

Strong Nitric-Sulfuric Acid Extract

The final extraction performed was basically that employed in the total assay analysis procedure. As the results tabulated as per cent total extracted mercury show (Table 3), this extract contained one-fourth to one-half of the total mercury of each sample.

Discussion of Phase Partitioning Results

The results of the phase partitionings are given in Tables 2 and 3. The limit of detection of the analytical procedure and apparatus used was 0.001 to 0.002 µg, and many of the values in this table were essentially close to this range. Negative values indicate loading by blank value mercury; i.e., the blank response exceeded the gross response. This loading was not too significant a factor, however, and only in the sodium hydroxide extraction series were these loadings of greater magnitude than analytical error.

TABLE 2

Results of phase determinations in ppm (dry weight basis), showing data corrected for reagent blank mercury.

Extract	B1, 0-10 cm	#I 60-70 cm	B2, 0-10 cm	#1 50-70 cm	GS32	GS1	Significance
Volatile Hg°	0.000	0.000	0.000	0.000	0.000	0.000	Volatile Hg°
1 N $MgCl_2$	0.000	0.000	0.000	0.000	0.003	0.000	Ion exchangeable Hg
0.2 N NaOH	0.017	0.000	0.114	0.004	0.331	0.206	Organic acids
0.005 N NaOH	0.185	0.172	0.342	0.160	0.841	1.136	Organic acids
0.005 N NaOH	0.000	0.000	0.000	0.000	0.000	0.000	Organic bases
Amalgamated Hg°	0.000	0.000	0.000	0.000	0.000	0.000	Amalgamated Hg°
Reducing soln.	0.000	0.000	0.000	0.000	0.021	0.002	Hydrous Fe oxides
Wash	0.020	0.024	0.029	0.028	0.020	0.027	Hydrous Fe oxides or small organics
Na_2EDTA	0.010	0.010	0.012	0.020	0.148	0.090	Small Fe-pptd. organics
Wash	0.020	0.016	0.025	0.012	0.059	0.049	Small Fe-pptd.
	0.020	0.014	0.025	0.000	0.039	0.046	organics
0.01% Dithio-threitol	0.013	0.006	0.024	0.012	0.068	0.056	Remaining organic Hg
HNO_3-H_2SO_4	0.242	0.078	0.933	0.087	1.162	1.984	Mainly sulfides, refractory organics
Grand Total	0.527	0.320	1.504	0.323	2.692	3.596	
Loadings	0.020	0.020	0.011	0.018	0.000	0.000	
Corrected Gr. Total	0.507	0.300	1.493	0.305	2.692	3.596	
Total Hg ASSAY	0.397	0.200	1.122	0.201	2.133	3.382	
Extra Hg found	0.110	0.100	0.371	0.173	0.559	0.214	
Recovery Percent	128%	150%	133%	149%	126%	106%	

TABLE 3

Results of phase determinations in per cent of uncorrected grand totals. The error due to loading is spread proportionately over the various components analyzed.

Extract	B1, 0-10 cm	#1 60-70 cm	B2, 0-10 cm	#1 50-70 cm	GS32	GS1	Significance
Volatile Hg°	0.0	0.0	0.0	0.0	0.0	0.0	Volatile Hg°
1 N $MgCl_2$	0.0	0.0	0.0	0.0	0.1	0.0	Ion exch. Hg
0.2 N NaOH	3.2	0.0	7.6	1.2	12.2	5.7	Organic acids
0.005 N NaOH	35.1	53.8	22.7	49.5	31.2	31.6	
0.005 N HOAc	0.0	0.0	0.0	0.0	0.0	0.0	Organic bases
Amalgamated Hg°	0.0	0.0	0.0	0.0	0.0	0.0	Amalgamated Hg°
Reducing soln.	0.0	0.0	0.0	0.0	1.0	0.1	Hydrous Fe oxides
Wash	3.8	7.5	1.9	8.7	0.9	0.8	Hydrous Fe oxides or small organics
Na_2EDTA + 2 washes	9.5	12.4	4.1	9.9	9.1	5.1	Small Fe-pptd. organics
0.01% Dithiothreitol	2.5	1.9	1.6	3.8	2.5	1.6	Remaining extractable organic Hg
HNO_3-H_2SO_4	45.9	24.4	62.1	26.9	43.1	55.1	Mainly sulfides, refractory organics
Total	100.0	100.0	100.0	100.0	100.0	100.0	

Table 2 is a short summary of the results reported in ppm (dry weight basis). The grand total values were calculated by ignoring the loadings; then corrected grand totals were calculated by subtracting the loadings from the grand total values. The summarized mercury values given in the main body of this table were not corrected for loadings due to the uncertainty of which phases present might have actually been responsible for the uptake of blank mercury.

Table 3 presents the data summarized as per cent values of the uncorrected grand totals. Calculated in this manner, the error due to loading is spread proportionately over the various analyzed components. The error due to blank mercury loading is small, anyway, being no larger than 6.7% of the corrected grand total in the worst case (B1, #1, 60-70 cm).

Comparison of the corrected grand total concentrations with the total mercury assays (data presented in Table 2) shows that the phase partitioning procedure detected 6% to 50% more total mercury. Since all six samples gave higher results by the partitioning method, rather than some giving lower results, it seems clear that a real difference of at least 10 to 30% exists between the two methods. Examination of Tables 2 and 3 failed to reveal any component or combination of components which might have roughly accounted for the extra mercury; in fact, the phase data seem to indicate that no mercury exists in phases not likely to yield mercury by the total assay procedure (such as hydrous iron oxides). Possibly, contact with some of the extracting reagents, particularly those with high pH, may have caused some sort of rearrangement within the

refractory phases and led to more complete solubilization in the final acid extraction. It is difficult to explain this "extra mercury" phenomenon otherwise.

The data summarized in Table 3 clearly show that three basic components account for nearly all of the mercury present in the samples. One-fourth to one-half of the mercury was bound to high molecular weight organic acids extractable in NaOH solutions. Most of this mercury component was soluble only in the dilute (0.005 N) NaOH solution, a probable consequence of the presence of significant numbers of basic functional groups on these mercury-bearing organic molecules. One to two-tenths of the total mercury appeared to be bound to smaller organic molecules which were soluble as far as in situ pH conditions were concerned, but were kept precipitated as insoluble complexes of some non-trace metal. The remaining one-fourth to one-half of the total mercury was extractable only by a strongly oxidizing mixture of concentrated nitric and sulfuric acids. Presumably this component includes mainly sulfides, plus any refractory organic compounds.

The most interesting implications concern the small, indirectly extracted organic molecules, which carried one to two-tenths of the total mercury. These are probably in large part degradation products of the larger ones extracted in the sodium hydroxide series. Table 3 shows that a greater percentage of the mercury associated with these occurred in the older, buried sediments than in their younger surface sediment counterparts. However, from Table 2 it is apparent that larger absolute quantities occurred in the surface sediments, probably due to

their much greater total mercury content. As no mercury was found in the surface waters, and almost none in the interstitial waters, and also due to the manner in which these molecules were extracted, it seems that some metal or metals were present in sufficiently large quantities to cause these molecules to remain as insoluble complexes, and thus effectively stifle their migration. It is unlikely that mercury is responsible for two reasons: 1) even in highly polluted sediments, the concentration of mercury is much lower than that of many other metals, and 2) since the organic molecules undoubtedly contained a number of different kinds of functional groups which were available for metal complexation, the mercury probably resided on the ones which had the greatest complexing power (especially sulfhydryl groups). Strohal and Huljev (1971) studied competitive interactions of other cations with mercury in bonding to humic acids, and found that although the reaction of mercury with these acids was slow, once completed no other cation was capable of displacing the mercury. Therefore the EDTA probably could not have removed the mercury from the organic molecules, as mercury-sulfhydryl bonding, and probably other mercury-organic functional group bonding, as well, would have been to stable for even the powerful chelator EDTA to break. Hence, some other metal is indicated.

It seems very likely that the metal which was keeping the smaller, otherwise soluble mercury-bearing organic molecules from going into solution was iron. This metal is present throughout Lake Erie bottom sediments in relatively high concentrations of 1 to 6% Fe, averaging 3.3 to 3.5% in the Western

and Central Basins and 2.7% in the Eastern Basin (Federal Water Pollution Control Administration (FWPCA), 1968). In addition, iron in these sediments shows a two- to threefold enrichment in the top of the sediment column as compared to concentrations at underlying depths. Therefore this metal is certainly present in large enough quantities to precipitate the otherwise soluble organic molecules as insoluble, mercury-bearing iron complexes. Chemically speaking, iron, especially in the trivalent ferric state, tends to have quite an affinity for the organic functional groups which are good complexing agents, especially those groups which are commonly found as constituents of proteins. In studies on the interactions of various metals with humic acids, Rashid and Leonard (1973) found that iron did have a high affinity for these organic acids. Therefore it seems clear that iron is both present in sufficient quantities and also has the necessary chemistry to behave in the proposed manner with regard to the smaller, more soluble mercury-loaded organic molecules. The enriched zone of iron in the upper several centimeters referred to earlier, be it due to cultural loading, post-burial mobilization, or both factors, would then tend to form a barrier to the upward migration of these otherwise soluble, mercury-bearing complexes. In light of the proposed mechanism, it would be especially interesting to perform measurements of methylation rate with the concentration of iron in the sediment as a variable. However, we know of no such studies which have been reported in the literature.

In view of the overall knowledge of the distribution of

mercury among the various components of Lake Erie bottom sediment, it is interesting to consider the likely effects of resuspension of such sediment with regard to behavior of the mercury. Such resuspension might take place by means of the actions of macrofauna, storm action, disturbances due to passing ships, or dredging activity. Any such resuspension would stir the sediment up into the more aerobic and biologically active overlying water mass. Here degradation of the various kinds of organics would proceed at a much more rapid rate, and a sharp increase in methylation would also likely occur. Sulfide phases containing mercury (hydrotroilite seems to be such a likely phase) would be subjected to at least partial oxidation and concomitant freeing of the mercury into aqueous solution. Despite the large amount of mercury that might be released in this manner, the overwhelming number of organic binding sites available in the water mass would almost certainly quickly take it back out of solution, so it is unlikely that serious water contamination would result. The danger that occurs hinges on the flux of released mercury which is incorporated into live organisms as opposed to that which finds itself attached to dead organic material and is quickly reburied.

There are several indications that such release of mercury might occur. Feick et al. (1972) performed artificial dredging experiments in aquaria containing mercury-contaminated sediment. They found that the mercury content of unfiltered water ranged from 0.208 to 1.66 mg/l, while filtered water samples gave readings of 0.8 to 5.6 µg/l. The major increase in the mercury content of the waters was then mainly due to mercury attached to

particulates, but a definite increase in dissolved mercury was also very apparent. Burkett (1973, pp. 64-65) reported high concentrations of mercury in the alga Cladophora in samples taken in Western Lake Erie in July of 1972, while several previous surveys had revealed much less mercury in this alga. He explained this anomalous increase on the basis of increased availability of mercury in the water due to severe storm action in the Great Lakes region related to the effects of Hurricane Agnes. This storm action had taken place only a few days before his July sampling expedition. Similarly, the dredging of a Finnish port was reported to have increased the soluble mercury concentration in the water to 10 µg/l from a previous value of 0.5 µg/l over a period of a few weeks (Stephan, 1971).

The apparent absence of some mercury-bearing phases which had been postulated to exist in bottom sediments merits some discussion here. First, there was apparently no metallic mercury, free or amalgamated, as had been proposed by Jenne (1970) and Bongers and Khattak (1972). If mercuric ions are strongly bound to organic functional groups, then such mercury would strongly resist reduction regardless of even extremely low redox potentials which might be present. Since sediment partitioning coefficients as low as 10^{-8} (ppm Hg in solution/ppm sediment on dry weight basis) have been measured by Feick et al. (1972), reduction of sediment mercury to Hg° seems very unlikely. Thus Eh-pH diagrams for inorganic systems, such as those presented by Hem (1970), are of very little value in understanding the behavior of mercury in sediments.

The apparent lack of mercury in hydrous iron or manganese

oxides is also significant, for if mercury were present in them to any important degree, diagenetic reduction of the iron or manganese would lead to dissolution of these solid phases and freeing of the contained mercury. Most of such released mercury would probably be taken up by the organic fractions anyway, but since many lake bottom sediments are especially rich in hydrous iron or manganese phases, such a mechanism could lead to considerable redistribution of contained mercury within the sediments, resulting in much mercury remaining near the sediment-water interface where it would be more likely to be absorbed by bottom feeders or stirred up into the overlying water mass.

The lack of mercury bound to organic bases is less noteworthy. In a lacustrine system, nearly all mercury is probably present in cationic forms (such as Hg^{++}, CH_3Hg^{+} , etc.), so one would not normally expect any degree of association with positively charged bases. Such an association might be important, however, in salt-water environments where much mercury might occur as the anion $HgCl_4^{--}$ due to the higher concentrations of chloride ion.

MERCURY, CHROMIUM, AND NICKEL ANALYSES OF LAKE ERIE SEDIMENT CORES

Sediment cores from throughout Lake Erie were collected on an eight-day cruise aboard the R/V INLAND SEAS during the period September 6-13, 1972. The cores were obtained by means of a gravity corer containing two-inch plastic liners. Twenty-one cores were selected from the suite obtained on this cruise for detailed analysis for mercury, nickel, and chromium. The

station locations are plotted in Figure 1. Further data concerning this cruise are available in Herdendorf (1972). All but four of these cores, 2-1, 5-2, 25-3, and 26-1 (the first number is the station number and the second identifies the core taken from a replicate set), consisted of muds and clays of various shades of gray. The other four consisted of sand or sand overlying clay.

Because previous studies in the Western Basin of the Lake have been developed in some detail (Kovacik, 1972; Walters et al., 1972; Walters and Herdendorf, 1973), it was deemed necessary later in this work to place the data gathered from the Western Basin cores of this study into the overall framework of the more extensive data for this area which was presented in the earlier studies. The samples used in those studies were taken during a cruise from July 19-29, 1971, aboard the R/B GS-1. The station locations for this cruise are given in Walters et al. (1972). Further information on the R/B GS-1 cruise may be found in Herdendorf (1971).

A short summary describing the physiography and geology of Lake Erie has been given by Kovacik (1972, pp. 5-11) and will not be repeated here. Much more detailed descriptions of the lake, especially with regard to chemical parameters, are given in FWPCA (1968) and IJC (1969). The surficial sediments of the lake have more recently been examined by Thomas et al. (1973). For the immediate purpose of this work it is important only to note that the lake is divided into three relatively shallow basins, the Western, Central, and Eastern, which are progressively deeper in that order. These are separated from

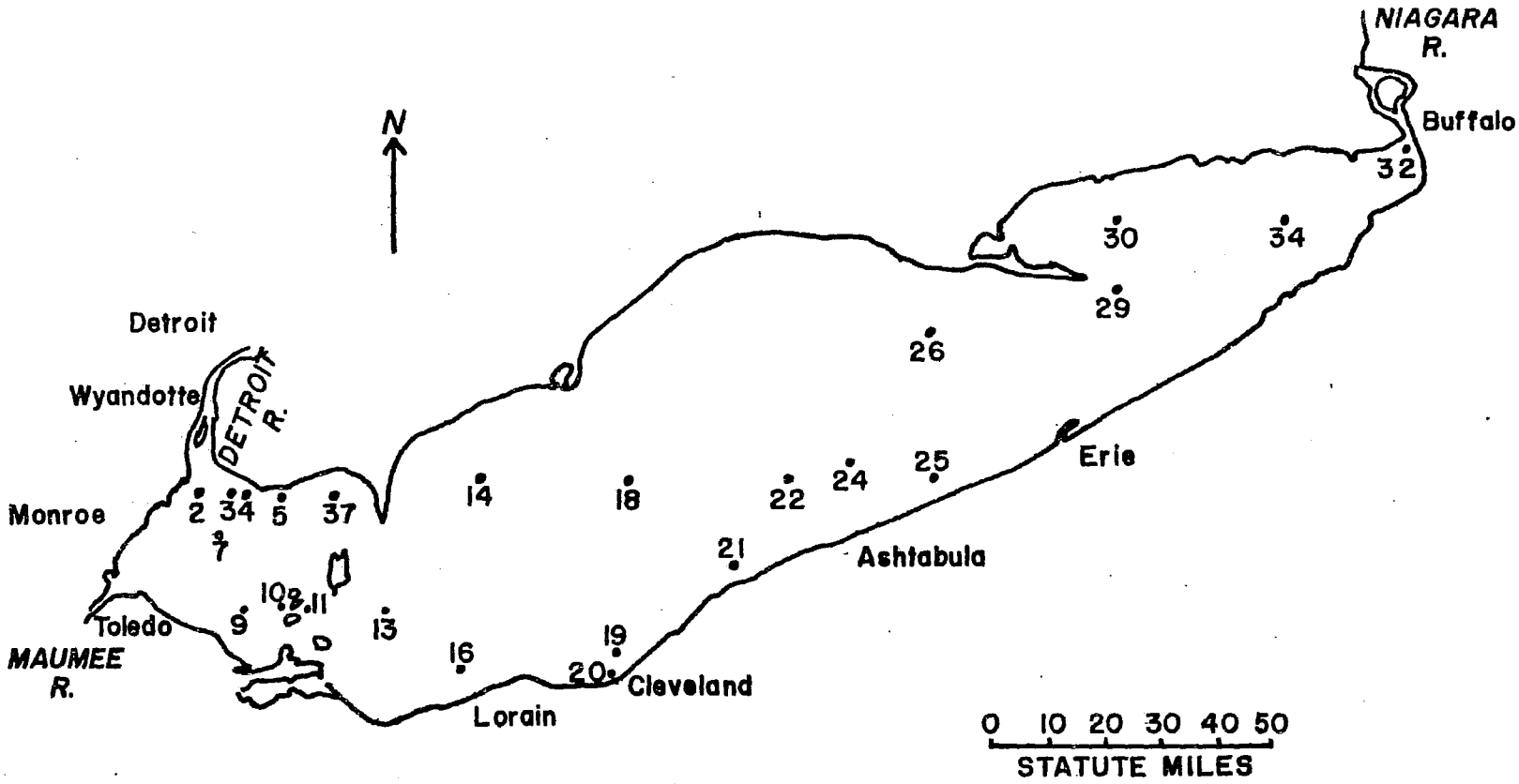

Figure 1. Map of Lake Erie showing station locations for cores analyzed in this study from the 1972 R/V INLAND SEAS cruise.

each other in turn by two sills, the Pelee-Loraine and the Long Point-Erie. The surficial sediments of the sills and nearshore areas are characterized by coarse sands and gravels of lag origin, while the basins themselves are composed of silty clays, clays, and muds (Thomas et al., 1973).

Analytical Procedures

Upon return to the laboratory, the sediment cores were subjected to an x-ray analysis procedure to determine porosity, sectioned into appropriate intervals, and stored frozen until time of analysis. At that time the samples were thawed and homogenized with a glass rod. Two one-gram portions were then taken, one for water determination and nickel-chromium analysis, the other for mercury analysis. The analytical procedure for mercury has been described in detail by Kovacik (1972, pp. 15-22). This procedure is a variation of the cold-vapor FAAS method of Hatch and Ott (1968).

The dried sediment samples used in the water determinations were extracted to remove non-silicate, non-anhydrous-oxide chromium and nickel. According to Burt (1973), this should include all of the sediment nickel within analytical error, but discriminate against a significant amount of the total chromium in the sediment. Because the data of Gibbs (1973) had indicated that most of the chromium present in unpolluted sediments was in crystalline solids (silicates and anhydrous oxides, mainly), it was felt that an analytical method which discriminated against these components, which are basically background components to begin with, would better serve the

purpose of this study.

A procedure based in part upon that of Presley et al. (1972) was devised. Seven ml of 30% H_2O_2 were added to each sample in a 50-ml beaker and allowed to react for 24 hours to oxidize the organic material and sulfides present. To insure complete reaction, three ml of 4 N HCl were added to each sample and heated carefully under low heating on a hotplate until all moisture was gone. Then five ml of 4 N HCl and 25 ml of 0.3 N hydroxylamine hydrochloride were added and the mixture was suspended using a rubber policeman. The sediment was then removed by centrifugation and the solution was stored in a clean two-ounce plastic bottle.

The solutions were analyzed for chromium and nickel by atomic absorption spectrometry on the same AAS unit as was the mercury, except that the unit was converted to the flame mode. The instrument settings and conditions of analysis were those given by Perkin-Elmer (1964). Standard solutions were made up in a manner parallel to that of the final sample solutions. The extracting reagents did not cause any serious interference, however. Some interference was known to have occurred because of the presence of iron, nickel, and copper in the samples (Vogliotti, 1970). The main problem was due to the large amounts of iron extracted, because, as noted earlier in this paper, Lake Erie sediments contain high levels of this metal. Experiments with iron-spiked standards showed that at the expected iron levels present, this interference caused a deviation of no more than 10%. This error is roughly equal to that occurring in the mercury analysis procedure, and was deemed

acceptable for the purposes of this study.

Results and Discussions

The results of the heavy metal analyses are similar to those obtained in some previous studies (Kennedy et al., 1971; Shimp et al., 1971; Kovacik, 1972). All three metals showed enrichment in the uppermost section of the sediment column, with fairly constant and lower background levels underlying the enriched section. No significant anomalous trends were detected in the depth profiles, although a small number of the cores did show only background values. The significance of these will be discussed later.

The data have been summarized in Table 4 in terms of geometric mean background values, surface concentration (metal contents of the top two cm of sediment), and sediment enrichment factors (SEF). The latter values were obtained by taking the ratios of the metal contents in the top two cm to the corresponding mean background values. The vast majority of cores showed signs of heavy metal enrichment. Only one core showed no mercury enrichment (26-1), and it showed signs of having had its uppermost section scoured off by means of some erosion process. Only three cores showed no signs of chromium pollution (26-1, 14-1, and 34-2), and five showed no signs of nickel enrichment (2-1, 14-1, 18-1, 32-2, and 34-2).

The degree of enrichment in the uppermost sections of the cores differed noticeably and systematically among the three metals and also among the three basins of the lake. Mercury was clearly the most enriched pollutant, having SEF values of

TABLE 4

Data summary of metal analyses in terms of geometric mean background values (B), concentration in the top two cm (P), and surface sediment enrichment factors (SEF).

Core no.	Mercury			Chromium			Nickel		
	B ppm	P ppm	SEF	B ppm	P ppm	SEF	B ppm	P ppm	SEF
2-1	0.026	0.41	16	21	66	3.1	27	37	1.4
3-1	0.018	2.1	110	15	143	9.5	56	112	2.0
4-1	0.053	2.0	39	13	87	6.7	27	67	2.5
5-2	0.060	1.4	23	14	88	6.3	50	79	1.6
7-2	0.060	2.8	46	19	141	7.4	65	144	2.2
9-2	0.065	1.4	21	19	80	4.2	80	138	1.7
10-1	0.033	0.71	21	17	75	4.4	45	84	1.9
11-2	0.023	0.82	39	17	48	2.8	43	67	1.6
13-2	0.030	0.44	15	18	37	2.1	50	65	1.3
14-1	0.030	0.12	4	24	18	0.8	48	39	0.8
37-1	0.045	1.0	22	13	47	3.6	33	76	2.3
16-1	0.027	0.3	12	19	60	3.2	24	56	2.3
18-1	0.026	0.18	9	32	47	1.5	42	35	0.8
19-1	0.025	0.46	18	14	53	3.8	43	95	2.2
20-1		0.93			149			90	
25-3		0.45		17	24	1.4			
26-1	0.019	0.014	0.74	21	5	0.3			
29-2	0.040	0.19	4.8	23	44	1.9	50	63	1.3
30-1	0.026	0.12	4.6				29	47	1.6
32-2	0.043	2.3	54	19	103	5.4	57	58	1.0
34-2	0.028	0.070	2.6	9	12	1.3	33	32	1.0

up to 114 (core 3-1), and typical ones of 20 to 30. Chromium was the next most enriched of the three metals, with its SEF values typically in the range of 2 to 7. Nickel showed very little enrichment, and most of its SEF values were in the range of 1 to 2. Geographically, the Western Basin seemed to have the highest typical SEF values for all three metals, except that it showed no greater trends in nickel enrichment than did the Central Basin. The Eastern Basin, excluding the core from the harbor at Buffalo, New York (32-2) clearly showed the least degree of enrichment for all three metals.

Mean background values varied from core to core, but they exhibited no detectable trends. For mercury these values ranged from 0.018 to 0.065 ppm (dry weight basis), although the overall range of background values was greater, being 0.010 to 0.14 ppm. The results closely match those of Kennedy et al. (1971), who found values of 0.03 to 0.06 ppm in a study of the bottom sediments of Lake Michigan. However, they are slightly lower than the values found by Kovacik (1972), who reported background values of 0.04 to 0.09 ppm in Western Lake Erie bottom sediments. Chromium and nickel mean background values were found to be 9.2 to 32 ppm and 24 to 80 ppm, respectively. Shimp et al. (1971) in a study of Lake Michigan bottom sediments found background values of 52 ppm and 35 ppm for chromium and nickel, respectively. The higher chromium background values in that study may reflect a real difference in the lake sediments or only a difference in analytical methods. FWQA (1970) reported chromium values in some Lake Erie sediments as low as 10 to 30 ppm, while the lower nickel values ranged from 20 to 40 ppm; these values are in better agreement with those obtained in this study.

The areal distribution of mercury, chromium and nickel in the surface 2 cm of sediment in Lake Erie is shown in Figures 2, 3, and 4 respectively. All three metals clearly show increasing gradients back to the source area--the Detroit River mouth. Some fifteen miles or so south of the mouth of the Detroit River the metal distribution patterns trifurcate into three distinct flows: 1) a minor eastward flow which follows a very narrow path until it spreads out in the area north of Pelee

Island; 2) a southern flow, also narrow, that fans out in the south-central part of the Western Basin; and 3) a southwest flow which slowly dies out as it approaches Toledo, Ohio. Although the control is sparse in the central and eastern basins, Cleveland seems to be a major source for chromium and nickel pollution that extends westward toward the western basin. Buffalo is also a source of chromium and nickel that is dispersed to the west. These dispersal patterns around Cleveland and Buffalo are in agreement with the clockwise bottom currents reported by FWPCA (1968, Figure 35, p. 73).

Depth Profiles from Harbors of Major Industrisl Centers

Core 32-2, Buffalo, New York

Core 32-2 was taken from the harbor of Buffalo, New York, one of the major industrial centers of Lake Erie. Since this location is right on the major outlet of Lake Erie, most of the pollutants entering the lake here are probably swept down the Niagara River into neighboring Lake Ontario. Porosity, mercury, chromium and nickel profiles are shown in Figure 5. All metal depth profiles given here and throughout the remainder of this work were plotted using logarithmic abscissas; porosity profiles are presented using normal linear coordinates.

Mercury and chromium and porosity all break sharply from background values at a depth of 23 cm, indicating a major sedimentologic discontinuity. The sediment samples were carefully examined with a hand lens to verify this conclusion. The sediment below 23 cm was a compacted, very plastic red (10R 3/2) clay intermixed with minor amounts of fine dolomitic gravel.

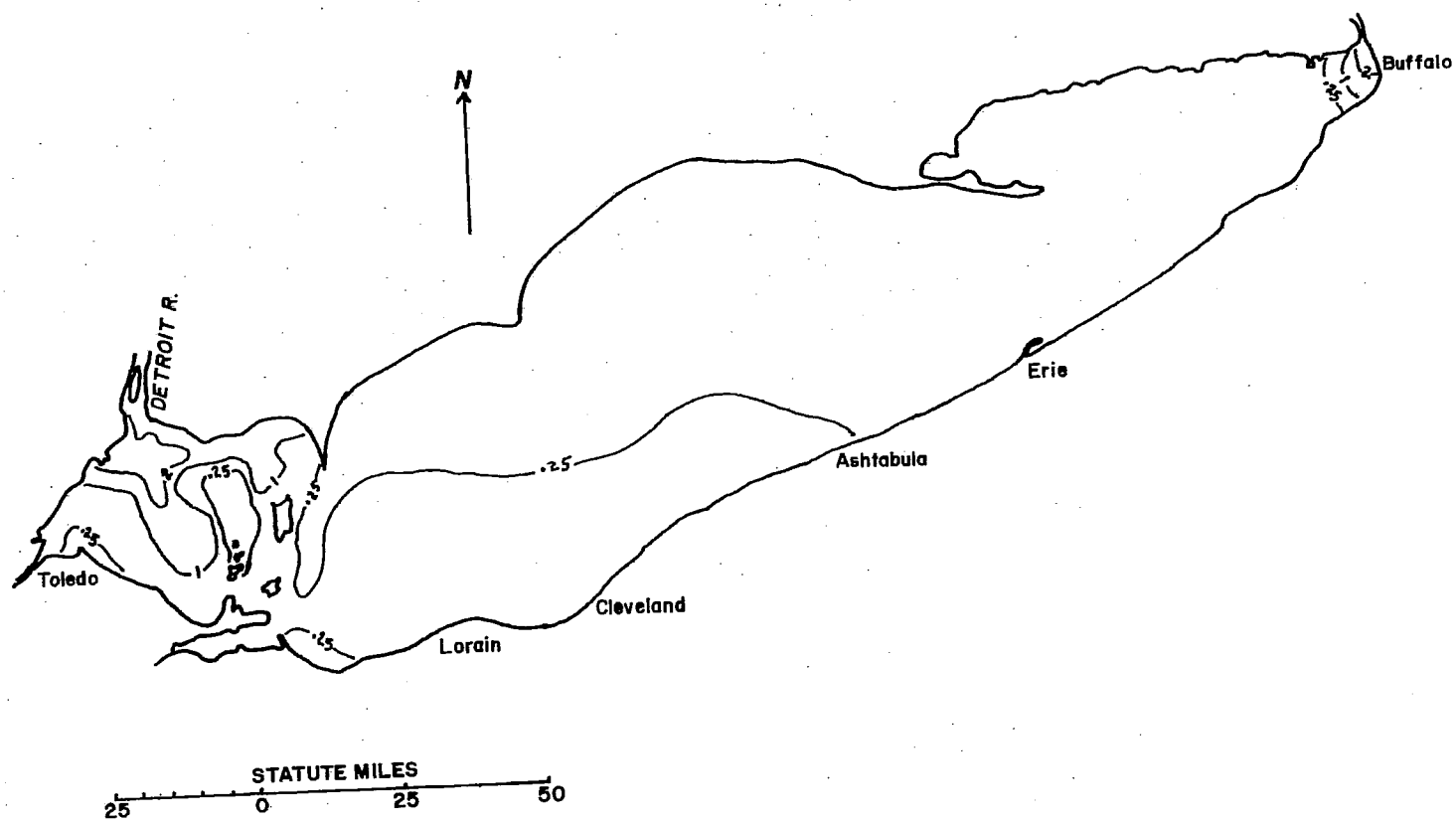

Figure 2. Map of mercury concentration in ppm in the top 2 cm of bottom sediment in Lake Erie.

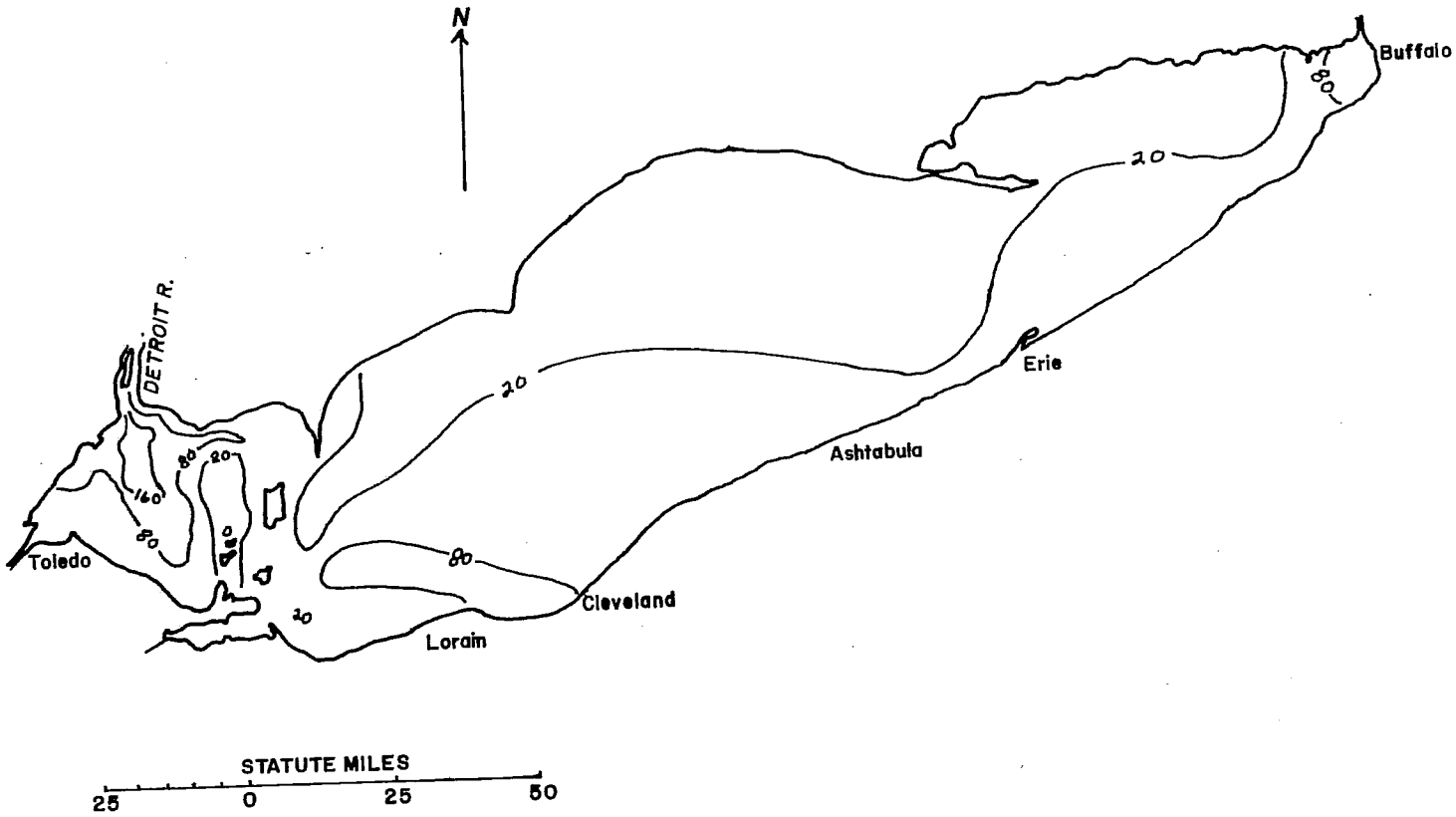

Figure 3. Map of chromium concentration in ppm in the top 2 cm of sediment in Lake Erie.

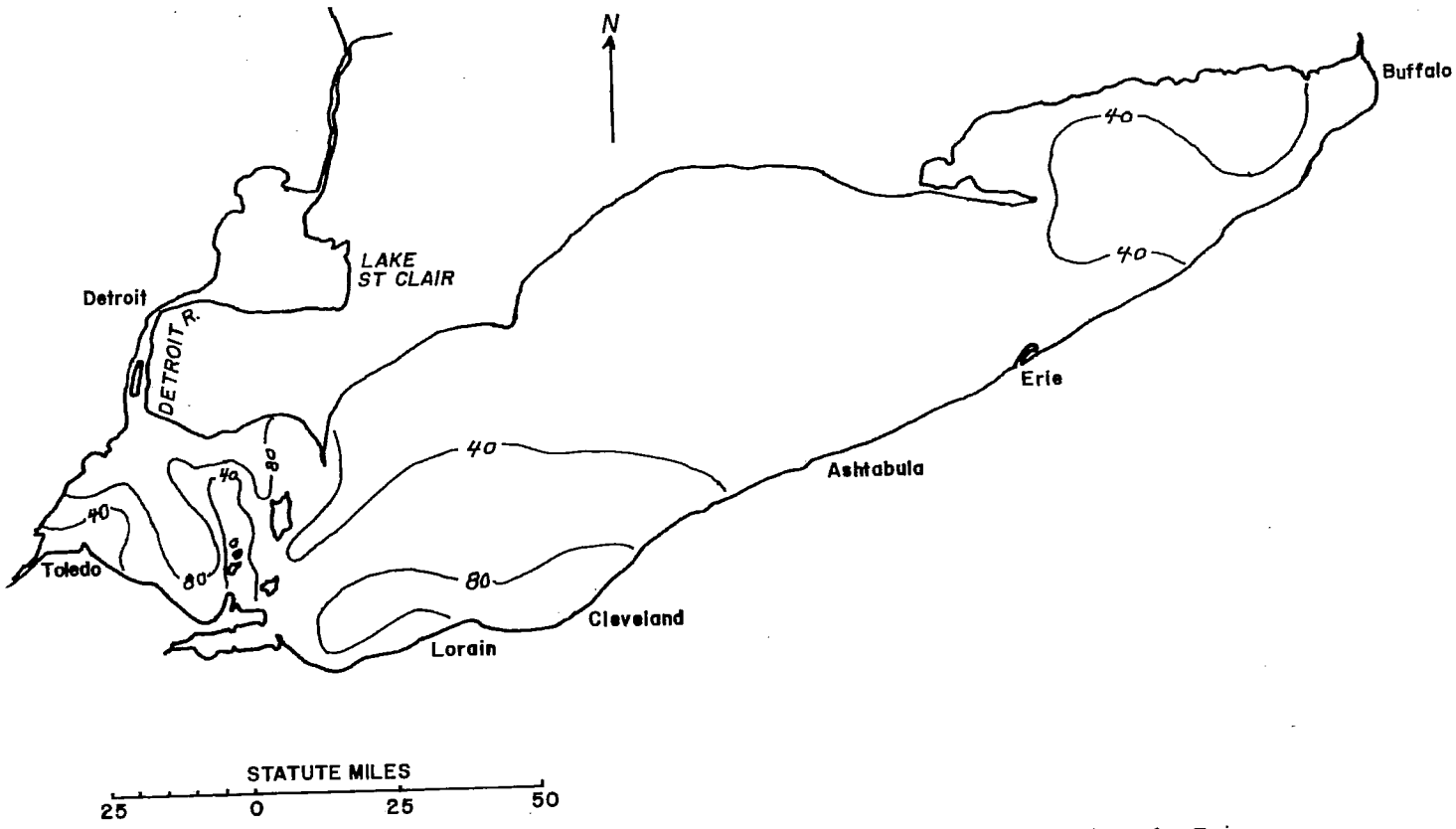

Figure 4. Map of nickel concentration in ppm in the top 2 cm of sediment in Lake Erie.

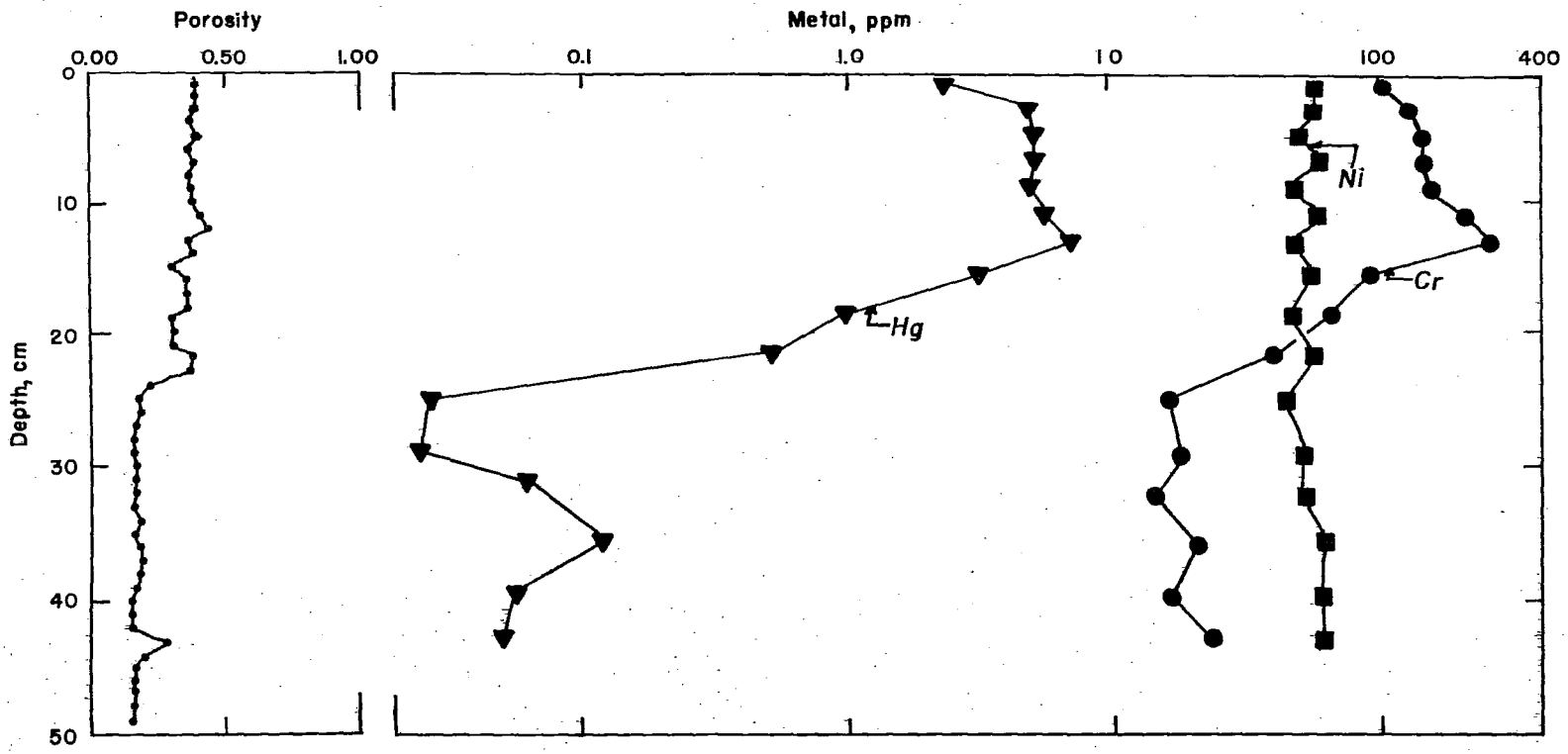

Figure 5. Depth profiles of porosity, mercury, chromium, and nickel for core 32-2.

that differences in the chemistry of the two metals would lead to differences in the appearance of the corresponding depth profiles. Thus, migration apparently did not occur for either metal. Nickel showed no variation within the core, its concentration remaining nearly constant throughout. If migration of nickel had occurred, we might expect that, due to the widely varying nature of the two zones of sediment, one would become enriched at the expense of the other. Therefore, no migration of nickel seems to have occurred either. The fairly well compacted nature of the upper zone of modern harbor sediment, however, suggests that it has been in its present position overlying the red clay for some time, on the order of several years at least. Therefore, if migration of the metals were indeed going to occur, it would probably have shown some signs of affecting the depth profiles by the time of collection of the core.

It is interesting to consider the possible sources of the pollutants found in this core. The mercury is so enriched that a major industrial source is suspected; the value of 6.94 ppm found in this core between 12 and 14 cm depth was the highest value obtained for a mercury content in this entire study. FWQA (1970) cited only one Buffalo industry as using mercury in industrial processes. This company, Allied Chemical Company, Buffalo Dye Division, was reportedly consuming 1560 lb/yr of mercury and discharging wastes to the Buffalo River (FWQA, 1970, p. 81). This mercury discharge is sufficiently large to explain the high concentrations found in the upper section of the harbor core (32-2), which was taken slightly north of the mouth of

chromium and nickel profiles would seem to rule out a recent, massive episode of resuspension-redeposition.

The constant mercury content may be due to an early source of pollution, not necessarily one of high magnitude, as was the case with the Buffalo core; a fluorescent light manufacturer has been operating in Cleveland since 1910, so this is a definite possibility. The chromium and nickel enrichment is undoubtedly due to the numerous (over 100) electroplating facilities in the Cleveland area. Steel plants may also have contributed to the nickel enrichment, which is of low magnitude.

Depth Profiles in the Eastern and Central Basins

Core 29-1, Eastern Basin

One core, 29-1, was taken from the deepest part of the lake in the Eastern Basin. Due to its location near the Central Basin and especially its being in the path of prevailing bottom flow from that Basin (FWPCA, 1968, Figure 35, p. 73) the content of this core was expected to be a record of heavy metal influx from the Central Basin into the Eastern Basin. A rate of surface sediment accumulation was calculated from post-glacial mud thickness data given by the International Joint Commission (IJC, 1969, Fig. 2.2.3, p. 60). The calculated rate was obtained by dividing the mud thickness by 12,000 years (IJC, 1969, p. 59) and correcting the rate so obtained to near-surface porosity. The average porosity of the upper section of the core was estimated to be 0.52; the average porosity of the entire mud column (4000 cm thick) was estimated to be close to 0.20 on the basis that this seemed to be a roughly limiting value in

some of the deeper cores of this study for which more complete porosity data were available. The calculated sedimentation rate for core 29-1 was then found to be

$$\frac{(4000 \text{ cm})}{(12{,}000 \text{ yr})} \times \frac{(0.52)}{(0.20)} = 0.86 \text{ cm/yr}$$

The application of this calculated rate is based on the assumption that sedimentation has been roughly constant and unchanged over the 12,000 yr post-glacial interval. Since the drainage basin around the Central and Eastern Basins is a fairly small area of moderate relief, it is believed that cultural factors have probably not increased this rate by more than twenty per cent. Overall, the error hopefully does not exceed twenty-five per cent, which is an acceptable value for the purposes here.

Figure 7 shows the depth profiles of merciry, nickel, and chromium for core 29-1 to a depth of 70 cm, and several selected dates calculated from the assumed sediment accumulation rate are also shown for purposes of discussion. From the turn of the century to the early forties there was perhaps a very minor increase in the mercury content, still well within normal background limits, however. As this time period was one of extensive coal burning, it is interesting to note that no significant record in the mercury profile has been produced, contrary to possible expectations based upon the work of Joensuu (1971). The mercury content had significantly increased by the late forties, however, and continued to increase to the time of collection of the core. This increase correlates well with the beginning of a new mercury-consuming industrial operation

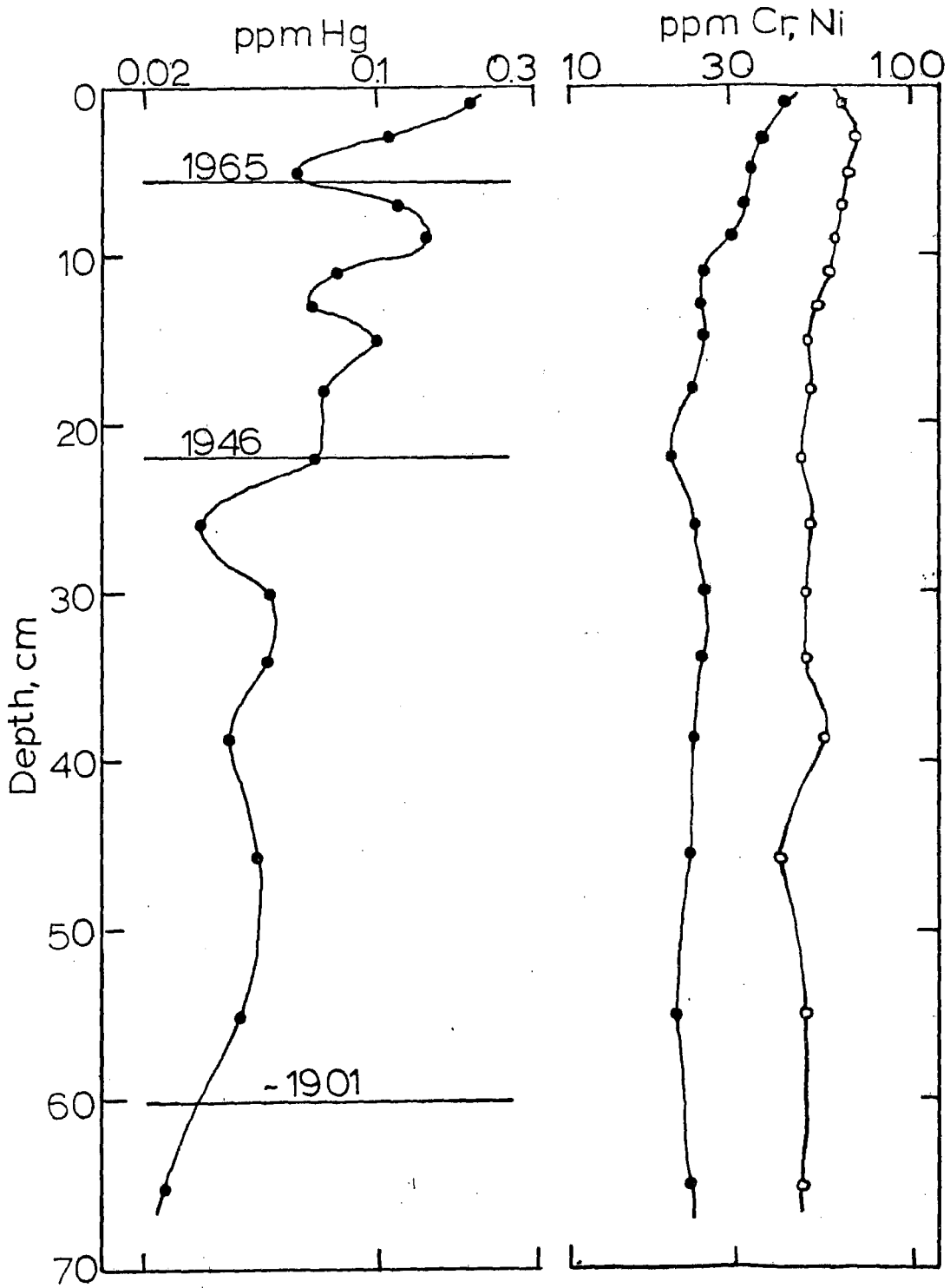

Figure 7. Depth profiles of mercury, chromium (●), and nickel (o) to 70 cm for core 29-1. Several dates calculated from the rate of surface sediment accumulation based on post-glacial mud thickness data of IJC (1969) are shown for purposes of discussion in the text.

in the city of Cleveland (a chemical plant established in 1946). Another increase in the late fifties correlates well with the opening of two mercury-consuming industrial plants in Northeast Ohio, one of which was a chlor-alkali plant using mercury cells (Detrex Chemical Industries, Inc., Ashtabula, Ohio, facility established in 1955). An extensive study of the Detrex plant has been reported by FWQA (1970), who cited it as consuming 9,120 lb Hg annually (p. 84). The Reactive Metals, Inc., titanium sponge plant, located in Ashtabula Township and established in 1957, was also suspected by FWQA (1970) of discharging mercury. A third increase in mercury seems to have occurred in the late sixties, paralleling the expansion of the Detrex facility in 1965. Chromium and nickel appeared to have undergone less drastic increases in the late forties, followed by more rapid increases in the late fifties. This interpretation correlates reasonably well with what little is known about the growth of the electroplating industry in the Cleveland area.

Core 18-1, Central Basin

Mercury, chromium, and nickel depth profiles for the top 60 cm of core 18-1 are plotted in Figure 8. A near-surface rate of sediment accumulation was calculated to be 0.31 cm/yr from the mud thickness data of IJC (1969) and assuming an effective porosity of 0.20 over the post-glacial mud column and a near-surface porosity of 0.55. As can be seen in Figure 8, mercury definitely began to increase in concentration by about 1947, correlating well with the 1946 establishment of the chemical plant in Clevelahd referred to earlier. Chromium showed a much

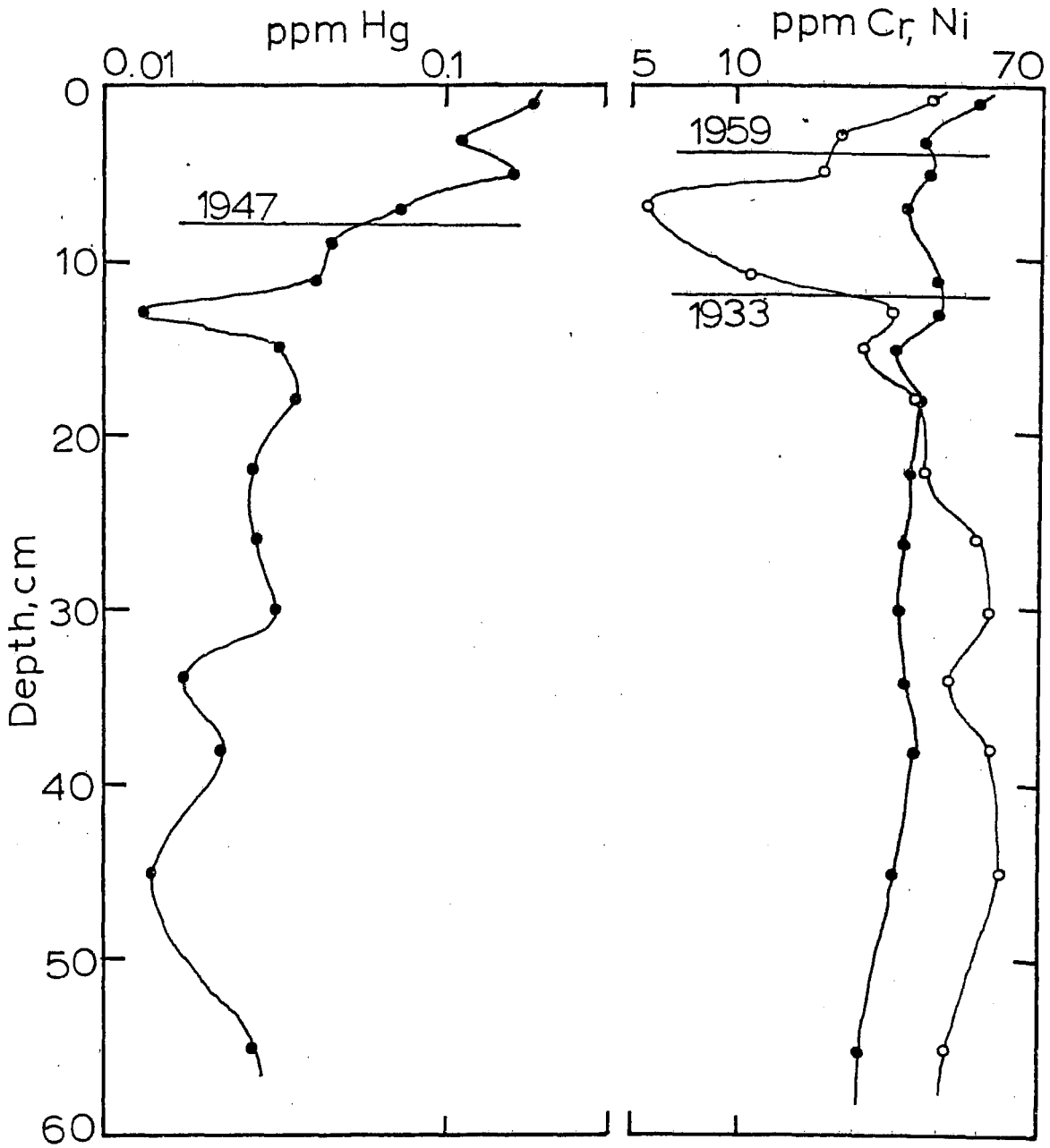

Figure 8. Depth profiles of mercury, chromium (●), and nickel (o) in the top 60 cm of core 18-1. Note the nickel-depleted zone corresponding to the time interval 1933-1959.

less pronounced rise in concentration which began in the early sixties. Nickel, however, shows the most interesting profile. Between 4 and 12 cm depth, a zone highly depleted in nickel exists. This zone corresponds in time to the period 1933-1959. It seems likely that this zone of nickel depletion is a consequence of the existence of an anoxic zone at the site of deposition during this time interval. Reducing conditions above the sediment-water interface could have led to the dissolution of hydrous iron oxides which otherwise would have been buried there. In the process, the contained nickel would have been lost to the water mass and carried elsewhere. Due to the sharp differences in the nature of this buried zone of depletion compared to its immediate surrounding, it seems unlikely that it could be anything other than a primary depositional feature.

Cores 13-2 and 14-1

Cores 13-2 and 14-1 were taken in the vicinity of the Pelee-Lorain sill which separates the Western and Central Basins. The features of these cores are very similar, and only the metal profiles for core 14-1 to a depth of 70 cm are shown in Figure 9. Mud thickness data from IJC (1969) were used with an assumed effective porosity of 0.20 over the entire post-glacial mud column along with surface porosities of 0.55 for each core, yielding values of 0.115 and 0.094 cm/yr for cores 13-2 and 14-1, respectively. The very shallow mercury break for core 14-1 at a little over 3.5 cm roughly corresponds to 1935. Within the relatively large error due to the shallowness of the pollution component, this value is in excellent agreement with the opening

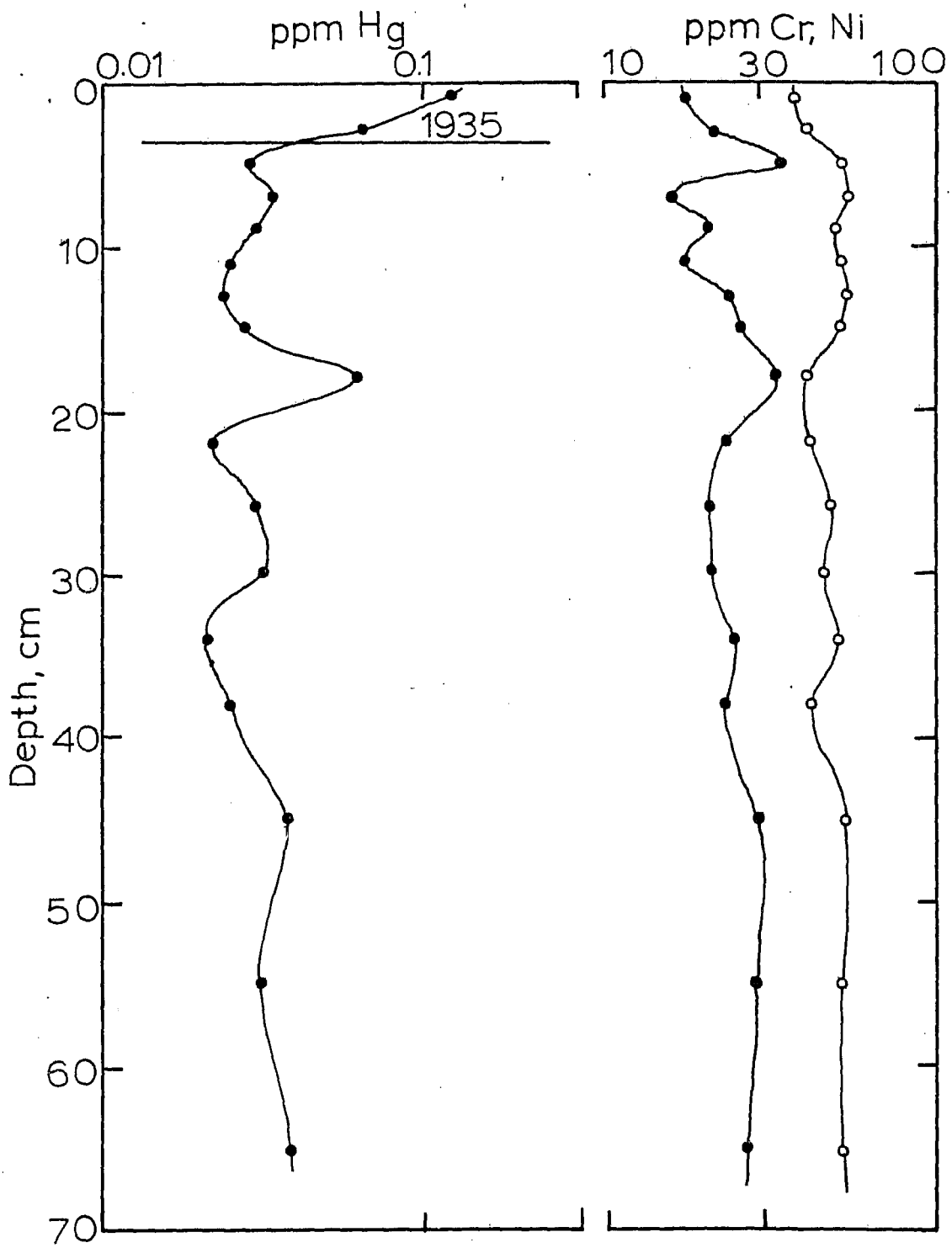

Figure 9. Depth profiles of mercury, chromium (●), and nickel (o) to a depth of 70 cm for core 14-1. The date of 1935 shown at the increase in mercury content was derived from a sedimentation rate of 0.094 cm/yr based on post-glacial mud thickness data of ITC (1969).

of the Wyandotte Chemical Corporation (then the Michigan Alkali Company) chlor-alkali plant at Wyandotte, Michigan in 1938-1939. A similar date of 1939 was obtained from core 13-2, also in excellent agreement with this source. These cores seem to indicate that mercury from the Wyandotte facility quickly reached across the Western Basin and effectively died out somewhere over the Pelee-Lorain sill. The enrichments of the mercury in these cores is very low compared with those farther west in the Western Basin.

Depth Profiles in the Western Basin

Dating of Lake Bottom Sediments by Means of Recent Mercury Accumulations

The rate of surface sediment accumulation is clearly a key factor in evaluating the effects of heavy metal pollution. The studies of Jernelov (1970) and Bongers and Khattak (1972) have pointed out that high rates of sedimentation significantly decrease methylation of mercury and its subsequent migration in methylated forms. In a more general sense, one might expect that any reactions leading to mobilization of any heavy metal pollutant would be less complete the faster the burial, since microbial populations quickly fall off with depth. In cases where there is a possibility of post-depositional migration of a heavy metal pollutant, knowledge of the rates of sediment accumulation may be essential, even critical, in evaluating and understanding the effects of abatement measures.

An especially convenient way of obtaining such rates in a heavy metal pollution study would be to use heavy metal accumulations themselves as time markers. Capuzzo and Anderson (1973)

have already utilized depth profiles of chromium in obtaining sedimentation rates in a river-estuary system, and the values they obtained were in excellent agreement with those obtained radiometrically. Obviously, certain criteria must be met if a particular heavy metal pollutant is to be successfully applied as a time marker in the sediments of a particular area. First, the metal should be highly enriched over background values, so a definite depth of initial accumulation of pollutant heavy metal (break-depth) can be pinpointed. Secondly, there must be sufficient historical control with regard to the sources of the pollutant metal. Ideally, these should be few in number so that there is little difficulty in matching concentration changes and industrial events. Also, the presence of more than one dating horizon allows the degree of internal consistency of the time frame to be tested, so two or three sources per metal is probably the optimum number. Thirdly, the metal used must not undergo more than minor post-depositional migration. This method, where applicable, possesses some advantage over most other methods, such as carbon-14 and Ambrosia dating, as the marker horizons are of much more recent age. Thus, it is unnecessary to make shaky extrapolations of assumed constancy of sedimentation to the more recent portions of the sediment column. Kemp et al. (1973) have shown that sedimentation rates in the Western Basin of Lake Erie have been significantly increased in recent years due to increased cultural activity. Therefore dating the sediments by means of pollutant metal horizons should yield more accurate data.

Only mercury of the three metals in this study is suitable

for precision dating of Western Basin bottom sediments. Nickel remains suspect of an unknown degree of post-depositional migration, its degree of enrichment gives poor contrast against the variation in background concentrations, and the historical control is very poor. Chromium, although otherwise excellently suited for dating purposes, is not suitable in the Western Basin of Lake Erie because the historical control is only moderately good. Assuming that the electroplating industry is the major source, chromium break-depths should correspond roughly somewhere within the period extending from the late thirties to the late forties, depending on the magnitude and variation of the local background. Mercury shows very high degrees of enrichment, post-depositional migration is probably minimal in view of the known high sedimentation rates in the Western Basin (Kemp et al., 1973), and the historical control is quite good.

There are already several indications that mercury dating can be performed successfully. In this study, correlation of mercury break-depths in core 19-1 with known industrial activity involving mercury in the Cleveland area gave good internal agreement, and the dates of mercury breaks in cores 13-2 and 14-1 matched well with the inception of the only probable source, the Wyandotte Chemical Corporation chlor-alkali facilities at Wyandotte, Michigan. In addition, Thomas (1972) presented a detailed depth profile of mercury in Lake Ontario. Pollen stratigraphy (using Ambrosia) placed the sharp increase in mercury in 1901, with a limit of error of roughly seven years either way. Thomas (1972) cited the Niagara River as the source area of this mercury, but he did not correlate it with any industrial event. However,

according to Haynes (1954, vol. I, p. 278), the first commercial chlor-alkali facility using mercury cells on the entire North American continent was that put into operation by the Mathieson Alkali Company at Niagara Falls, New York in 1897. These Mathieson cells had a loss rate of 0.5 lb Hg/ton Cl_2 (Mantell, 1950, p. 408). Needless to say, the correlation between the opening of this facility and the date obtained by Thomas (1972) for the initial input of mercury into Lake Ontario is astoundingly good.

The nine cores taken from the Western Basin on the September 1972 cruise of the R/V INLAND SEAS were examined with the express intent of dating them via pollutant mercury horizons. Two dating horizons were expected to be available, subject to the ability to discern one from the other in cores with very low sedimentation rates. The first major break should have occurred in 1939, the first year of operation of mercury cell chlor-alkali facilities of the Michigan Alkali Company at Wyandotte, Michigan. These facilities were completed in 1938 (Wyandotte Chemical Corporation, 1961, p. 21); for dating purposes an extra year was allowed for the plant to come on-stream and for the mercury to spread down the Detroit River into Lake Erie and across the Western Basin. Cores 13-2 and 14-1, as noted earlier in this work, indicated that the Wyandotte mercury spread quickly across the Western Basin to the Pelee-Lorain sill, but sedimentation of this mercury essentially confined it within the Western Basin. Cores taken from the Central Basin appeared not to show any responses due to the input of mercury from this source, so the spillover into the Central Basin was apparently negligible. If

Cline et al. (1973) were correct that mercury travels in low specific gravity organic flocs, then the speed of dispersal across the Basin could well have been sufficient to have caused the observed mercury increases in the cores from the sill area roughly within the first year of operation of the Michigan Alkali Company's mercury cells. A second and apparently much larger pollutant mercury increase was expected due to construction in 1953 of a second plant built in Wyandotte by the same company, now the Wyandotte Chemical Corporation (Industrial and Engineering Chemistry, 1954, p. 53A). Again, for dating purposes, an extra year was allowed for the plant to come on-stream and the mercury to spread throughout the Basin.

All of the Western Basin cores except 3-1, 5-2, and 10-1 clearly showed the two expected breaks. The second breaks in cores 3-1 and 4-1 were ill-defined. Only three data points above the single observed break were available for core 5-2, so a second break could not have been distinguished even if it were present. For all Western Basin cores and core 13-2, the initial mercury break was taken as marking the 1939 time horizon. Then assuming constancy of sedimentation rates above this horizon, dates were determined for the second mercury break, which was expected to fall somewhere in the period from the late forties to the late fifties. In this manner it was possible to provide some measure of an internal check on the method. Rates of surface sediment accumulation were calculated for all of these cores using the 1939 horizon as the time marking horizon.

Porosity and heavy metal depth profiles for the upper 50 cm of core 9-2 are presented in Figure 10. The porosity profile

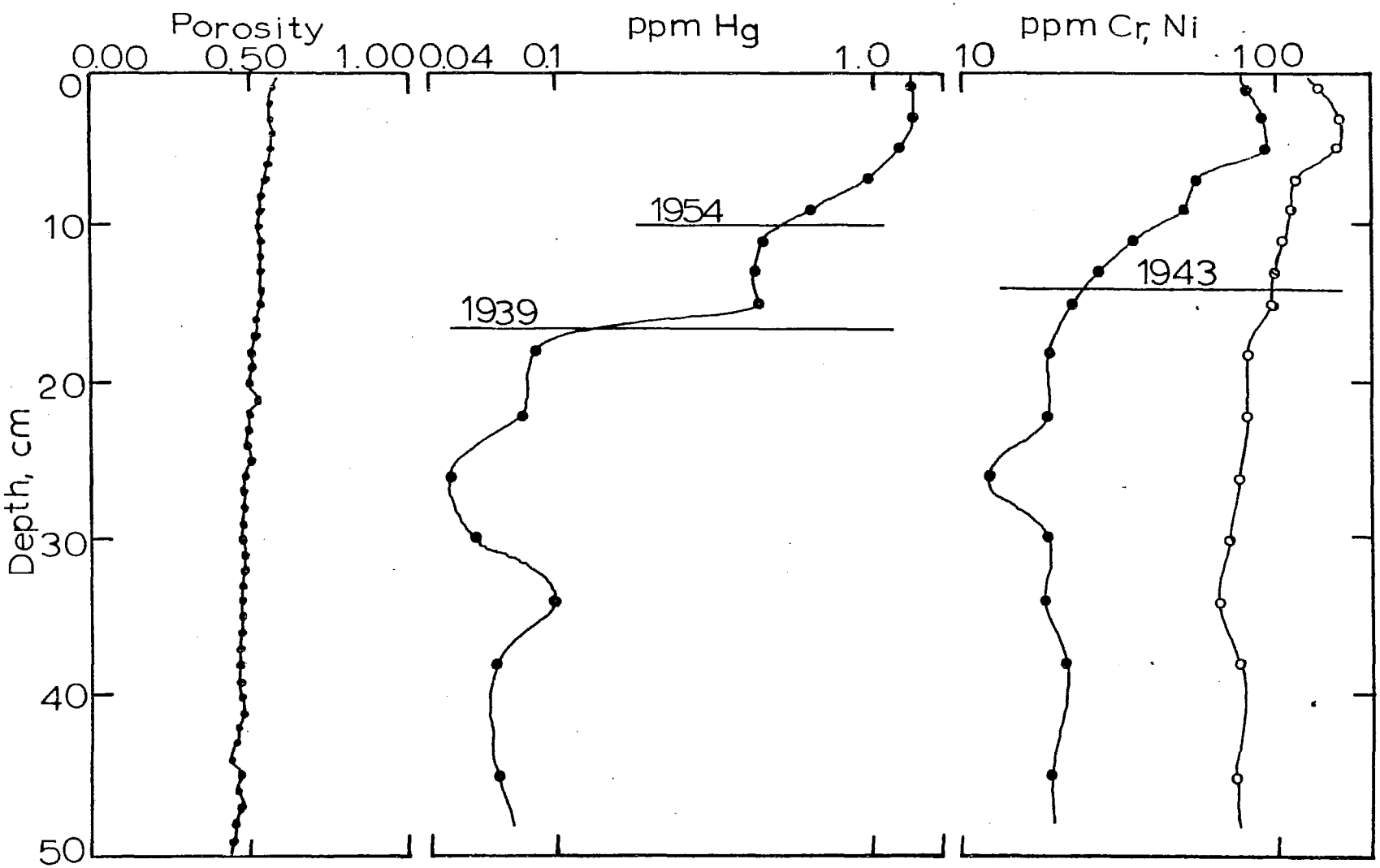

Figure 10. Depth profiles of porosity, mercury, chromium (●), and nickel (o) in the top 50 cm of core 9-2. The dates shown are based on taking the first major break-depth of mercury as the 1939 horizon. The second mercury break at a depth of 10 cm is very prominent in this core.

showed no signs of discontinuities in the sedimentation on these intervals, there being only a mild, even degree of compaction with increasing depth. The dates obtained for the second mercury breaks were 1954 for core 9-2 and 1956 for core 4-1, in excellent agreement with the expected date of 1954.

Table 5 summarizes the calculated sedimentation rates and times of major metal increases for all Western Basin cores and core 13-2. In general, there is good agreement within each of the cores, with the conspicuous exception of core 2-1, which showed both the chromium and the second mercury breaks occurring in 1962. These breaks coincide, however, with a contact between underlying mud and an underlying sandier sediment. This contact may well mark a depositional hiatus, which would easily explain the late dates obtained. Core 7-2 gave a rather late date of 1953 for its chromium break, which coincided with the second mercury break. This chromium break was unusually sharp, suggesting that the break occurred immediately above a horizon of a depositional hiatus. The porosity log for this core gave no evidence of such a hiatus; possibly, however, one might have occurred but was not recorded in the porosity profile due to a lack of noticeable compaction in the underlying material.

The cores immediately around the Islands area of the Western Basin (cores 7-2, 9-2, 10-1, and 11-2) contained a rather porous, peat-rich zone at depths below about a meter and a half. The peaty zone extended from 167 to 180 cm and was overlain and underlain by a hard, compacted clay. A more diffuse zone of peat-rich mud occurred from roughly 125 to 160 cm. Two buried mercury peaks correspond to these zones. Chromium showed a

TABLE 5

Sedimentation rates and calculated dates of major metal influx (based on the 1939 horizon) for Western Basin cores of the 6-13 September 1972 cruise of the R/V INLAND SEAS

Core no.	Sedimentation rate, cm/yr	Date of the second Hg break	Date of the Cr break
2-1	0.24	1962	1962
3-1	1.51	1955	1940
4-1	1.30	1956	1949
5-2	0.21		1943
7-2	0.73	1953	1953
9-2	0.50	1954	1939
10-1	0.44	1952	1938
11-2	0.33	1957	1947
13-2	0.30	1957	1939
37-1	0.24	1955	1939

lesser positive correlation with them, while nickel showed a very weak negative correlation. These results are in general accord with the known geochemistries of these metals, with mercury and chromium tending to occur with organic material while nickel does not. The sharpness of the buried mercury peaks offers further evidence that mercury depth profiles in Lake Erie are primary depositional features which are not significantly altered by diagenesis.

Kovacik (1972) analyzed a large number of cores taken in the Western Basin on a five-minute latitude-longitude grid pattern. He determined the mercury contents of about five or six depth intervals per core, most of the analyses being conducted in the upper several centimeters. This data was used to calculate the rates of surface sediment accumulation for these cores. The results are given in Table 6. Nearly all of the data

were calculated using the 1939 horizon. Some had to be calculated from the 1954 horizon (second mercury break-depth) due to high sedimentation rates and consequent lack of control at the 1939 horizon using Kovacik's data; these rates based on the 1954 horizon are marked by parentheses in Table 6. The error in most of these numbers is estimated to be within 15%; a very few numbers may be in error up to 25% owing to lack of precise control around the break-depths.

The data of Tables 5 and 6 were combined in Figure 11. The pattern of sediment distribution is revealed by the map of rates of surface sediment accumulations. The pattern in general parallels that of the metal distributions, except that the major influx of sediment is clearly coming from the Maumee River, while the smaller sediment load from the Detroit River is deposited mainly in an area close to the river mouth, giving rise to the highest sedimentation rates in the Western Basin (up to 1.51 cm/yr). These relative sediment influxes are in accord with USGS data presented by Dept. of Interior (1970, vol. I, p. 315); these data showed the Maumee River basin as contributing 1,179,000 tons per year of sediment of which 1,159,000 tons per year was attributed to sheet erosion. The total sediment load of the Maumee River made up over half of the total sediment influx into the Western Basin from the United States. Since sheet erosion is in large part a cultural phenomenon, it is not surprising that Kemp et al. (1973) found that sedimentation rates in the Western Basin have greatly increased in recent, cultural times. The sediment being deposited north of Pelee Island is not derived from influx of river sediment, but rather is a product of tremendous

TABLE 6

Rates of surface sediment accumulation in the Western Basin of Lake Erie, calculated from the data of Kovacik (1972); data in parantheses were determined using the 1954 mercury break, others by the 1939 break.

Core no.	Sedimentation rate, cm/yr	Core no	Sedimentation rate, cm/yr
1	0.88	32	0.00
1A		33	0.45
2	(0.53)	34	0.24
2A	(0.17)	35	(0.60)
3	0.29	36	0.40
4	0.61	37	0.91
5	0.58	38	0.61
6	0.39	39	
7		40	0.00
8	0.46	41	
9	0.46	42	
10	0.90	43	0.50
11	0.00	44	0.73
12	0.00	45	0.00
13	0.20	46	0.46
14	0.32	47	0.30
15	0.45	48	0.12
16	(0.55)	49	0.00
17		50	
18	0.17	51	0.00
19	0.18	52	0.55
20	0.12	53	0.21
21		54	
22	0.64	55	0.60
23	0.11	56	(0.22)
24	0.00	57	
25	0.46	58	0.00
26	(0.11)	59	0.09
27		60	0.24
28	0.06	61	0.61
29	(0.06)	62	0.30
30		D-1	(1.05)
31	0.06	D-2	(0.76)

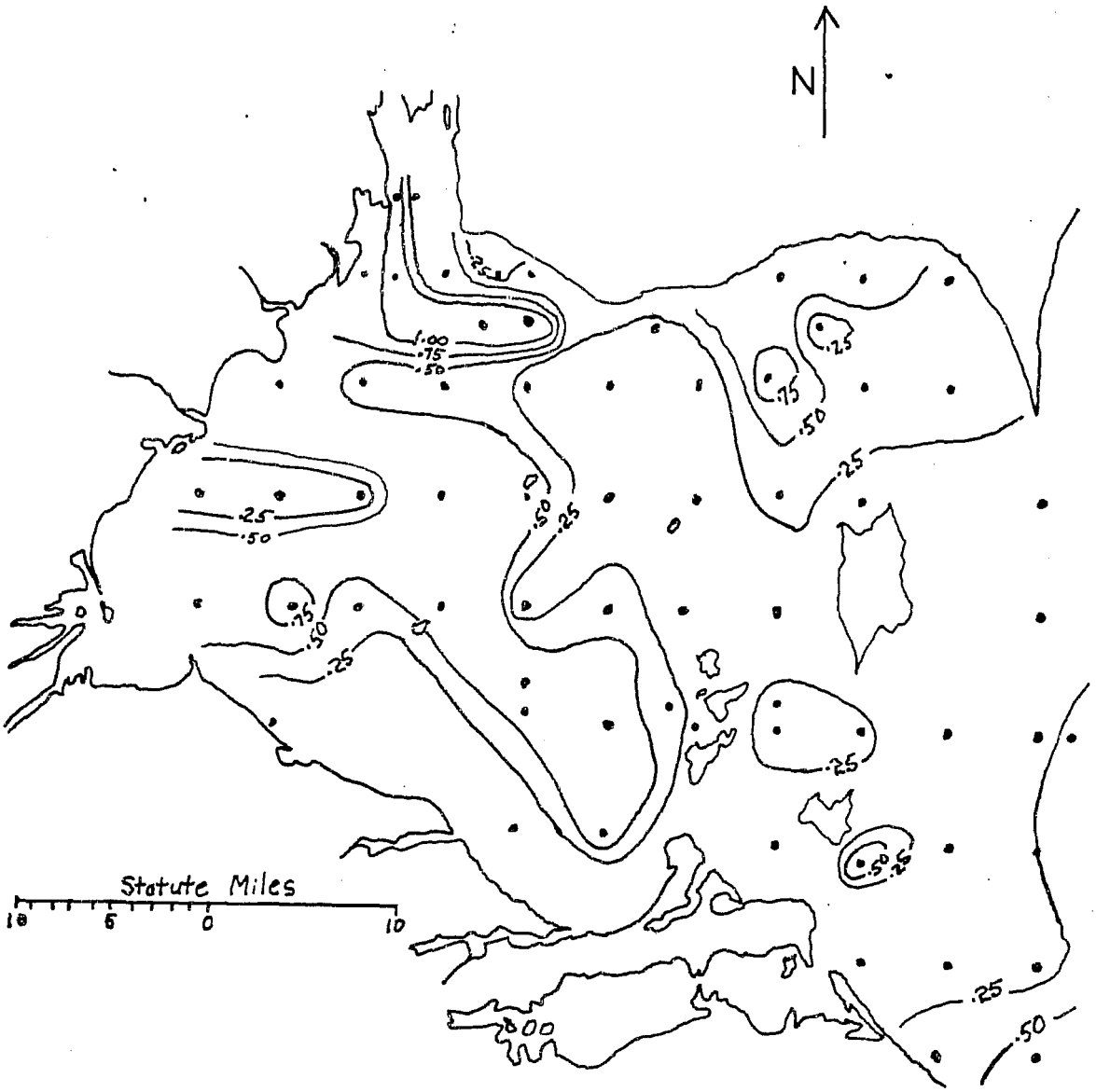

Figure 11. Map of recent sedimentation rates (cm/yr) in the Western Basin obtained from mercury data of Kovacik (1972) and this work, based on the initial introduction of mercury pollution into the Western Basin in 1939. Note the large flux of sediment coming from the Maumee River. Control is indicated by the station locations (●).

shore erosion on the adjacent Canadian shore (see Coakley, 1972; and Coakley and Cho, 1972). The large areas of high sedimentation of the metals in this area and in the south-central part of the Basin are primarily due to mixing of pollutant loads of the metals from the Detroit River into the sediment from the Canadian shore erosion and the Maumee River sediment load, respectively. Two minor areas of high sedimentation rates and high heavy metal concentrations occur east of Kelly's Island and the Bass Islands, respectively. These are likely due to more quiet zones favorable to the sedimentation of fine organic and hydrous ferric oxide particles in the shelter of the islands from prevailing bottom currents. Another minor area of such high values is about twenty miles east-northeast of Toledo and is believed to represent another quiet area which lies in the "eye" of a vortex in the prevailing bottom currents (see FWPCA, 1968).

The sedimentation rate data indicate a rather large area of erosion and/or nondeposition exists in the middle of the Western Basin. This zone extends from the Bass Islands north to within five miles or so of the Canadian shore. Its width is about five miles throughout most of its length, but increases to about eight miles as it approaches the Canadian shore (see Fig. 11).

It is interesting in view of the available data to ask which are the "worst" areas in the Western Basin with regard to mercury and what remedial measures, if any, ought to be taken. Certainly the gravest threat lies not in the actual mercury concentrations in the bottom sediments, but rather the amounts

of mercury that may be expected to migrate across the sediment-water interface into the main water mass where large portions may then enter the lake biomass. As noted earlier, the removal of even a small fraction of bottom-sediment-mercury via post-depositional migration may result in undesirably high concentrations of the metal in that portion of the biomass which is high on the ladder of food-chain concentration processes.

Several factors besides the sedimentation rate act to determine the amount of mercury which is remobilized in a thin layer of sediment. Perhaps the two factors which are next in importance are 1) presence of burrowing macrofauna, including type of macrofauna, and 2) the proportion of mercury in the layer which will, through time, be converted from methylatable, organically bound mercury to the nonmethylatable sulfide form. From the work of Jernelöv (1970), it appears that the presence of burrowing clams presents the worst case with regard to macrofauna. Here the loss rate is slightly less than for the presence of sludge worms (0.3%/yr as opposed to 0.5%/yr), but the depth to cessation of methylation is increased from 3 cm to 10 cm. Assuming a sedimentation rate of 0.1 cm/yr which appears to be a minimum value for areas of active sedimentation in the Western Basin of Lake Erie, the amount remobilized would be 30% of the total original mercury. This amount, may be regarded as an upper limit to the proportion of remobilized, methylated mercury. The data in this work indicate that just about half of the mercury in contaminated sediments is apparently bound in sulfides and hence not available for methylation (provided the sediment is not severely disturbed, as by storm action

or dredging). Thus, it seems more likely that the maximum percentage of remobilized mercury for Western Basin bottom sediments would be more in the range of 8 percent (sludge worms) to fifteen percent (burrowing clams).

The above calculations indicate that the amount of remobilized mercury should be roughly proportional to the initial mercury concentration and inversely proportional to the rate of sediment accumulation. From the limited data available, it appears that the proportion of sulfide-bound mercury does not vary much (43 to 62 percent) in contaminated sediment, although precultural sediments have a smaller proportion, just about 25 percent. To determine the areas where the most mercury should be remobilized now that the industrial sources have been essentially turned off, a map of relative methylmercury flux factors (RMMFF), defined as

RMMFF = ppm Hg (dry weight basis)/sedimentation rate, cm/yr,

was constructed for the Western Basin of Lake Erie. A mercury content of 0.1 ppm and a sedimentation rate of 0.1 cm/yr represent the highest likely background mercury content and the lowest sedimentation rate likely to occur in the Western Basin, and these indicate that their ratio, an RMMFF value of 1.0, would be an approximate limit for background RMMFF values in this Basin.

The RMMFF map in Figure 12 shows a very different distribution pattern than either the sedimentation rate map (Fig. 11) or the bottom sediment mercury map (Fig. 2). The major area of high values (RMMFF $\geq$ 6) occurs some twelve miles south of the

mouth of the Detroit River in a narrow belt running nearly east-west. A smaller area of such high RMMFF values occurs some ten miles northwest of the Bass Islands. These areas represent fairly localized areas where the threat is greatest from the production of methylated mercury in the years to come, and are here pointed out mainly as target areas for future research. Quantitative methylation studies similar to those of Langley (1973) would be particularly useful in determining future courses of action concerning these areas. Possibly it may be necessary to cover the bottom sediments in these areas with fine gravel (Bongers and Khattak, 1972). At present, however, it may be premature to decide on such measures, as continued high inputs of sediment into the Western Basin may well suffice to eliminate the mercury hazard.

NEUTRON ACTIVATION ANALYSIS OF LAKE ERIE SEDIMENTS

Previous determinations of trace metals in Lake Erie sediments by Zubkoff and Carey (1970) were limited in scope because an instrumental method of analysis was used in conjunction with a 3" x 3" NaI(Tl) detector system. The objective of this phase of our study was to develop a reliable neutron activation analysis method for a potentially significant suite of heavy metals employing the readily available NaI(Tl) detector systems. The procedure of Santos and Walters (1971), which was based on chemical separation then gamma ray spectrometry, was modified and tested to achieve this objective.

The basic procedure of Santos and Walters (1971) was designed for trace metals in sulfide minerals. Lake Erie sediments,

sediment cores. The abundance of iron (0.8-3.8%) is great enough that it behaves as a major element. The iron content of the sediments are more related to sediment type than the trace elements.

TABLE 7

Neutron activation analysis results

Core	Depth Interval	Co ppm	Cu ppm	Zn ppm	Sb ppm	Fe ppm
32-2	0-2	17	59	270	0.86	22000
	8-10	13	91	230	-	28000
	17-20	11	41	190	0.28	25000
	23-27	9.2	14	-	0.15	12000
	48-55	10	18	13	-	14000
20-1	0-1	21	110	660	2.4	37000
	59-69	21	110	750	2.1	38000
	113-121	16	58	300	-	30000
	121-125	9.3	15	-	0.16	18000
34-2	0-2	9.9	14	58	-	14000
	2-4	8.8	11	48	-	12000
	75.5-80	6.6	8.5	19	0.28	9600
	254-260	7.3	14	38	0.04	19000
4-1	0-2	11	58	260	0.09	22000
	6-8	15	74	200	-	24000
	16-20	14	54	100	0.78	21000
	24-28	12	38	68	0.14	18000
	32-36	8.9	15	4.5	0.88	14000
	50-54	6.9	6.3	49	0.18	10000
	54-60	7.9	7.8	44	2.0	12000
	60-66	7.0	8.7	41	0.80	7800

The geochemical coherence of the trace elements is lost in some instances due to the independent sources of pollutants. Antimony is highest in core 20-1 from Cleveland harbor. Much lower levels were observed for cores 32-2 from Buffalo harbor, 34-2 from the eastern basin and core 4-1 from the western basin.

Generally cobalt, copper and zinc are present in the same proportions. The background values of these elements are about 8 ppm Co, 10 ppm Cu, and 45 ppm Zn. The parallelism between the trace elements and iron may be due to a control of trace element mobility by the precipitation of organic complexes with iron. This hypothesis warrants further investigation.

SUMMARY OF MAJOR RESULTS

Phase distribution analyses for mercury in Lake Erie water and sediment samples revealed that most of the mercury is bound to organic sediment fractions. Dissolved mercury in surface microlayer and bulk surface water samples was less than the detection limit (~0.02 µg/l). Interstitial waters contained mercury in a range from less than the detection limit up to 0.06 µg/l. Among the solid constituents the mercury was essentially contained in three components: 1) cold-extractable organic acids (30 to 54 per cent); 2) indirectly-extracted small iron(?)-organic complexes (5 to 20 per cent); and 3) sulfides plus refractory organics, if any. Other previously postulated forms were found to be either not detectable or present in very small concentrations, such as volatile metallic mercury (not detected), ion-exchangeable mercury ($\leq$0.1 per cent), mercury in hydrated metallic oxides ($\leq$1.9 per cent), mercury on organic bases (not detected), and mercury amalgamated to iron oxides (not detected).

Detailed depth profiles for mercury, nickel, and chromium revealed that in Lake Erie the Western Basin surface sediments are the most highly enriched in all three metals, and the

Eastern Basin sediments the least enriched. Mercury enrichment varied up to 114 times background levels, while enrichment factors for chromium were typically 2-7 and for nickel typically 1-2. In general, it was found that very few profiles fit well to an exponential model. Rather, a definite approach to near-steady state concentrations seemed to be evident, punctuated by secondary increases which appeared to be related, in some cases at least, to specific industrial events.

A high degree of historical control on the input of mercury into the Western Basin, combined with the presence of known high rates of sedimentation, made this area ideal for sediment dating by means of pollutant mercury accumulations. Modern sedimentation rates were calculated using the mercury data of this study and that of Kovacik (1972). The distribution of these calculated rates clearly shows that the Maumee River is the major source of sediment input, in agreement with previously known data. The Detroit River input, although smaller in volume, is essentially "dumped" in a small area just south of the river mouth and gives rise to sedimentation rates as high as 1.51 cm/yr. A thrid major source of sediment is coming from the Canadian shore, and area of severe shoreline erosion. Small, local highs of sedimentation occur in partially sheltered areas east of the Bass Islands and Kelly's Island, and in the "eye" of a vortex of bottom current patterns east of Toledo, Ohio. A high correlation existed among the three metals, the bottom current patterns, and the obtained pattern of sedimentation, except that the major input of all three metals was clearly coming from

the Detroit River. A large area of erosion and/or deposition was found extending from the Bass Islands north to within five miles of the Canadian shore. This zone varied from five to eight miles in width.

The effect of sedimentation rate on the remobilization of sedimented mercury via methylation was examined using a simplified model based on the work of Jernelöv (1970). Two major areas were delineated where large amounts of mercury could potentially be remobilized through time: 1) a linear belt some fifteen miles long and three to six miles wide running nearly east-west, located some five miles south of the Detroit River and 2) a smaller area, roughly five miles in diameter, roughly ten miles northwest of South Bass Island. The percentage of remobilized mercury in these areas is likely to be from 8 to 15 per cent of the total pollutant mercury now within 10 cm of the sediment-water interface. Further study of these areas is crucial to determining what remedial measures, if any, may be necessary. The high sedimentation in most of the remainder of the Western Basin is probably sufficient to eliminate the mercury hazard there without need of any such measures.

Neutron activation analysis of Co, Cu, Zn, Sb, and Fe in 4 sediment cores indicated that these elements are also concentrated in an enriched zone at the sediment surface. Although there is some degree of variability among the various trace elements measured, it seems that there is a basic process that controls the abundance of these trace elements.

The detailed depth profiles of Hg, Cr, and Ni do not support a diffusion controlled mechanism to explain the increase in these

elements at the sediment-water interface. Therefore we conclude that cultural loading is primarily responsible for the depth-concentration profiles observed. Since mercury does not appear to be migrating within the sediment column, we recommend that the sediments not be distributed unless absolutely necessary.

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REFERENCES

Bernheim, F., 1971, The effect of cyanogen idodid and mercuric chloride on the permeability of cells of Pseudo-monas aeruginosa and the antagonistic action of sulfhydryl compounds: Proc. Soc. Experimental Biology and Medicine, v. 138, p. 444-447.

Bongers, L.H., and M.N. Khattak, 1972, Sand and gravel overlay for control of mercury in sediments: U.S. Environmental Protection Agency, Washington, D.C., 45 p.

Burkett, R.D., 1973, The use of Cladophora to monitor mercury occurrence in western Lake Erie waters: Unpublished Ph.D. thesis, The Ohio State University, Columbus, Ohio, 84 p.

Burt, N.E., 1973, The analysis of chromium and nickel in lake waters and lake bottom sediments: Unpublished M.A. thesis, Bowling Green State University, Bowling Green, Ohio, 74 p.

Capuzzo, J.M., and F.E. Anderson, 1973, The use of modern chromium accumulations to determine estuarine sedimentation rates: Marine Geology, v. 14, p. 225-235.

Chau, Y.K., and H. Saitoh, 1973, Distribution of mercury in the Great Lakes: Presentation before the 16th Conf. Great Lakes Res.

Cline, J.T., and S.B. Upchurch, 1973, Mode of heavy-metal concentration in the upper strata of lake sediments: Proc. 16th Conf. Great Lakes Res. (in press).

Cline, J.T., J.L. Hillson, and S.B. Upchurch, 1973, Mercury mobilization as an organic complex: Proc. 16th Conf. Great Lakes Res. (in press).

Coakley, J.P., 1972, Nearshore sediment studies in western Lake Erie: Proc. 15th Conf. Great Lakes Res., p. 330-343.

Coakley, J.P., and H.K. Cho, 1972, Shore erosion in western Lake Erie: Proc. 15th Conf. Great Lakes Res., p. 344-360.

Cranston, R.E., and D.E. Buckley, 1972, Mercury pathways in a river and estuary: Environ. Sci. and Technol., v. 6, p. 274-278.

Dept. of Interior, 1972, Proc. Conf. in the matter of pollution of Lake Erie and its tributaries, 5th Session, 609 p.

D'Itri, F.M., 1972, Source of mercury in the environment: in Environmental Mercury Contamination (p. 5-25), edited by Rolf Hartung and B.D. Dinman, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 349 p.

Fagerström, T., and A. Jernelöv, 1972, Some aspects of the quantitative ecology of mercury: Water Research, v. 6, p. 1193-1202.

Federal Water Pollution Control Administration, 1968, Lake Erie Environmental Summary 1963-1964: U.S. Dept. of the Interior, Washington, D.C., 170 p.

Federal Water Quality Administration, 1970, Investigations of mercury in the St. Clair River-Lake Erie systems: Open-file report, 108 p.

Feick, G., E.E. Johanson, and D.S. Yeaple, 1972, Control of mercury contamination in freshwater sediments: U.S. Environmental Protection Agency, Washington, D.C., 156 p.

Gibbs, R.J., 1973, Mechanisms of trace metal transport in rivers: Science, v. 180, p. 71-73.

Hatch, W.R., and W.L. Ott, 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Anal. Chem., v. 40, p. 2085-2087.

Haynes, W., 1954, American Chemical Industry, vol. I: D. Van Nostrand, New York, 512 p.

Hem, J.D., 1970, Chemical behavior of mercury in aqueous media: Geological Survey Professional Paper 713, p. 19-24.

Herdendorf, C.E., 1971, Preliminary cruise data research vessel GS-1 July 19-29, 1971: Unpublished report, no pagination.

Herdendorf, C.E., 1972, Lake Erie limnology cruise aboard the R/V INLAND SEAS September 6-13, 1972--preliminary results: Center for Lake Erie Area Research, The Ohio State University, Columbus, Ohio 127 p.

Hoover, C.R., and J.W. Masselli, 1941, Disposal of waste liquors from chromium plating: Industrial and Engineering Chemistry, v. 33, p. 131-134.

Industrial and Engineering Chemistry, 1954, Chemical progress in 1953: Industrial and Engineering Chemistry, v. 46, p. 11A-57A.

International Joint Commission, 1969, Pollution of Lake Erie, Lake Ontario, and the International Section of the St. Lawrence River, vol. II--Lake Erie: International Joint Commission, 316 p.

Jenne, E.A., 1970, Atmospheric and fluvial transport of mercury: Geological Survey Professional Paper 713, p. 40-45.

Jensen, S., and A. Jernelöv, 1967, Biosyntes av metylkvicksilver. I. Nordforsk Biocindenformation, v. 10, p. 4-5.

Jensen, S., and A. Jernelöv, 1968, Biosyntes av metylkvicksilver. II. Bildning av dimetylkvicksilver: Nordforsk Biocindinformation, v. 10, p. 4-5.

Jensen, S., and A. Jernelöv, 1969, Biological methylation of mercury in aquatic organisms: Nature, v. 233, p. 753-754.

Jernelöv, A., 1970, Release of methyl mercury from sediments with layers containing inorganic mercury at different depths: Limnology and Oceanography, v. 15, p. 958-960.

Joensuu, O., 1971, Fossil fuels as a source of mercury pollution: Science, v. 172, p. 1027-1028.

Kennedy, E.J., R.R. Ruch, and N.F. Shimp, 1971, Distribution of mercury in unconsolidated sediments from southern Lake Michigan: Illinois State Geological Survey, Environmental Geology Notes, no. 44, 18 p.

Kemp, A.L.W., R.L. Thomas, T.W. Anderson, and A. Mudrochova, 1973, Sedimentation rates and recent sediment history of Lakes Ontario, Erie, and Huron: Presentation before 16th Conf. Great Lakes Res.

Kirk-Othmer Encyclopedia of Chemical Technology, 1947, vol. III: The Interscience Encyclopedia, Inc., New York, 955 p.

Kovacik, T.L., 1972, Distribution of mercury in western Lake Erie waters: Unpublished M.A. thesis, Bowling Green State University, Bowling Green, Ohio, 74 p.

Kovacik, T.L., and L.J. Walters, Jr., 1973, Mercury distribution in sediment cores from western Lake Erie: Proc. 16th Conf. Great Lakes Res. (in press).

Krenkel, P.A., 1973, Mercury: environmental considerations, part I.: CRC Critical Reviews in Environmental Control, v. 3, p. 303-373.

Langley, D.G., 1973, Mercury methylation in an aquatic environment: Jour. Water Pollution Control Federation, v. 45, p. 44-51.

Mantell, C.L., 1950, Industrial Electrochemistry, 3rd ed.: McGraw-Hill, New York, 781 p.

Meade, R.H., 1966, Factors influencing the early stages of the compaction of clays and sands--review: Jour. Sediment. Petrol., v. 36, p. 1085-1101.

Ontario Water Resources Commission, 1970, Report on the mercury pollution of the St. Clair River system: Open-file report, 57 p.

Perkin-Elmer, 1964, Analytical methods for atomic absorption spectrophotometry: Perkin-Elmer, Norwalk, Connecticut, no pagination.

Presley, B.J., Y. Kolodny, A. Nissenbaum, and I.R. Kaplan, 1972, Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia--II. Trace element distribution in interstitial water and sediment: Geochim. Cosmochim. Acta, v. 36, p. 1073-1090.

Rashid, M.A., and J.D. Leonard, 1973, Modifications in the solubility and precipitation behavior of various metals as a result of their interaction with sedimentary humic acid: Chemical Geology, v. 11, p. 89-97.

Santos, G.G., Jr., and L.J. Walters, Jr., 1971, Gold Provinces in the Philippines defined by activation analysis. P. 143-156 in Nuclear Techniques for mineral exploration and exploitation, International Atomic Energy Agency, Vienna.

Shimp, N.F., J.A. Schleicher, R.R. Ruch, D.B. Heck, and H.V. Leland, 1971, Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan: Illinois State Geological Survey, Environmental Geology Notes, no. 41, 25 p.

Stephan, D.G., 1971, Trip report--Finland and Sweden, Feb. 21-25, 1971, in Problem of mercury emissions into the environment of the United States: U.S. Environmental Protection Agency, Washington, D.C.

Strohal, P., and D. Huljev, 1971, Investigation of mercury-pollutant interaction with humic acids by means of radiotracers: Proc. Nuclear Techniques in Environmental Pollution, International Atomic Energy Commission, Vienna, p. 439-446.

Study Group on Mercury Hazards, 1971, Hazards of mercury: Environmental Research, v. 4, 69 p.

Thomas, R.L., 1972, The distribution of mercury in the sediments of Lake Ontario: Canadian Jour. Earth Science, v. 9, p. 636-651.

Thomas, R.L., A.L.W. Kemp, and C.F.M. Lewis, 1973, The surficial sediments of Lake Erie: Oral presentation, 16th Conf. Great Lakes Res.

Vernet, J.-P., and R.L. Thomas, 1972a, The occurrence and distribution of mercury in the sediments of the Petit Lac (Western Lake Geneva): Eclogae Geologicae Helvetiae, v. 65, 307-316.

Vogliotti, F.L., 1970, The atomic absorption determination of chromium in the presence of aluminum, cobalt, iron, copper, and nickel: Atomic Absorption Newsletter, v. 9, p. 123-124.

Walters, L.J., Jr., C.E. Herdendorf, L.J. Charlesworth, Jr., H.K. Anders, W.B. Jackson, E.J. Skoch, D.K. Webb, T.L. Kovacik, and C.S. Sikes, 1972, Mercury contamination and its relation to other physico-chemical parameters in the western basin of Lake Erie: Proc. 15th Conf. Great Lakes Res., p. 306-316.

Walters, L.J., Jr., and C.E. Herdendorf, 1973, Mercury concentrations in surface sediments as related to water masses in western Lake Erie: Compass, v. 50, p. 5-10.

Weiss, H.V., M. Koide, and E.D. Goldberg, 1971, Mercury in a Greenland ice sheet: evidence of recent input by man: Science, v. 174, p. 692-694.

Wood, J.M., F.S. Kennedy, and C.G. Rosen, 1968, Synthesis of methyl-mercury compounds by extracts of a methanogenic bacterium: Nature, v. 220, p. 173-174.

Wyandotte Chemical Corporation, 1961, Caustic Soda: Wyandotte Chemical Corporation, Wyandotte, Michigan, 144 p.

Zubkoff, P.L., and W.E. Carey, 1970, Neutron activation analysis of sediments in western Lake Erie, Proc. 13th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res., p. 319-325.